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ABSTRACT

Knoff, Mark Robert. Ph.D., Purdue University, August 1999. Enhanced Nitrification in Constructed Wetlands using Ion-exchange and Biological Regeneration. Major Professor: Ronald F. Wukasch.

Constructed wetlands built in northern climates do not adequately remove nitrogen, especially ammoniacal nitrogen, in the winter. Clinoptilolite, an ion-exchange crystal, can be used to store ammonium from wetland effluents during the colder winter months when nitrification is limited by environmental constraints. The ammonium-sorbed clinoptilolite can be biologically regenerated during the summer months, when conditions are more conducive for nitrification. Laboratory scale and pilot scale studies were conducted to prove this hypothesis and develop design criteria for a clinoptilolite supplemental system. Ultimately, two small pilot scale clinoptilolite columns were built that utilized an in-situ nitrifying biomass (*Nitrosomonas* and *Nitrobacter*) and draw and fill technology. The study showed that ammonium-sorbed clinoptilolite can be bioregenerated using tap water, an in-situ nitrifying biomass, and draw and fill aeration. The process can remove almost 100% of the adsorbed ammonium. The nitrifying biomass can remove at least 94% of the ammonium as nitrate at ambient temperatures as low as 14°C. Oxygen utilization is extremely efficient in the draw and fill bioregeneration scheme. The nitrifying biomass utilized from 68 - 95% of the available oxygen to oxidize the ammonium adsorbed by the clinoptilolite during the initial stages of regeneration. In practice, a clinoptilolite bed system will reduce constructed wetland design requirements. The design can be optimized for year-round BOD removal and summer-time nitrogen removal which will reduce the CW size under normal municipal waste conditions. Theoretically, a clinoptilolite bed system coupled with a CW system can be used to remove almost 100% of the wetland's effluent ammonia during the six month adsorption phase. After the ammonia is converted to nitrate, the nitrate can be used to decrease the influent BOD concentration into the CW. Overall, this study shows that it is feasible to use a clinoptilolite based system to adsorb ammonium in temperatures typically found during the winter months and biologically regenerate the ammonium-sorbed clinoptilolite using a low-strength cation regenerant with an in-situ nitrifying biomass and draw and fill aeration.

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ABSTRACT

Knoff, Mark Robert. Ph.D., Purdue University, August 1999. Enhanced Nitrification in Constructed Wetlands using Ion-exchange and Biological Regeneration. Major Professor: Ronald F. Wukasch.

Constructed wetlands built in northern climates do not adequately remove nitrogen, especially ammoniacal nitrogen, in the winter. Clinoptilolite, an ion-exchange crystal, can be used to store ammonium from wetland effluents during the colder winter months when nitrification is limited by environmental constraints. The ammonium-sorbed clinoptilolite can be biologically regenerated during the summer months, when conditions are more conducive for nitrification. Laboratory scale and pilot scale studies were conducted to prove this hypothesis and develop design criteria for a clinoptilolite supplemental system. Ultimately, two small pilot scale clinoptilolite columns were built that utilized an in-situ nitrifying biomass (*Nitrosomonas* and *Nitrobacter*) and draw and fill technology. The study showed that ammonium-sorbed clinoptilolite can be bioregenerated using tap water, an in-situ nitrifying biomass, and draw and fill aeration. The process can remove almost 100% of the adsorbed ammonium. The nitrifying biomass can remove at least 94% of the ammonium as nitrate at ambient temperatures as low as 14°C. Oxygen utilization is extremely efficient in the draw and fill bioregeneration scheme. The nitrifying biomass utilized from 68 - 95% of the available oxygen to oxidize the ammonium adsorbed by the clinoptilolite during the initial stages of regeneration. In practice, a clinoptilolite bed system will reduce constructed wetland design requirements. The design can be optimized for year-round BOD removal and summer-time nitrogen removal which will reduce the CW size under normal municipal waste conditions. Theoretically, a clinoptilolite bed system coupled with a CW system can be used to remove almost 100% of the wetland's effluent ammonia during the six month adsorption phase. After the ammonia is converted to nitrate, the nitrate can be used to decrease the influent BOD concentration into the CW. Overall, this study shows

that it is feasible to use a clinoptilolite based system to adsorb ammonium in temperatures typically found during the winter months and biologically regenerate the ammonium-sorbed clinoptilolite using a low-strength cation regenerant with an in-situ nitrifying biomass and draw and fill aeration.

CHAPTER 1
INTRODUCTION

1.1 Research Objective

The objective of this study was to investigate the applicability of enhancing nitrification in constructed wetlands systems using ion-exchange and biological regeneration, specifically in temperate climates. The study focused on the feasibility of using a zeolite, clinoptilolite, to chemically store ammonium in cold temperatures and regenerate the ammonium-sorbed clinoptilolite biologically under conditions that are more conducive for nitrification. The experiments were designed so that the data gathered during the investigation could be used to design a clinoptilolite-enhanced wetland system.

1.2 Problem Statement

1.2.1 Poor Nitrogen Removal

Constructed wetlands (CWs) used to treat various waste streams are becoming more prevalent in the United States. CWs require minimal capital costs compared to other conventional treatment processes, and are also easier to construct and maintain (Brix, 1987). Besides these benefits, most CWs that treat organic wastes adequately remove variable loadings of organic material, such as 5-day biochemical oxygen demand (BOD_5), total suspended solids (TSS), and fecal coliform (Hammer and Knight, 1994; Brown and Reed, 1994; Kaldec, 1995). However, most CW designs may not adequately remove nitrogen (Kemp and George, 1997; Reed and Brown, 1995; White, 1995). In fact, Brix (1987), reported removal efficiencies for nitrogen of less than 30% for the majority of CWs he studied. In a study of 14 constructed wetlands, Reed and

Brown (1995), determined that half of the wetlands had a net production and export of ammonia.

1.2.2 Reasons for Poor Nitrogen Removal

There are two main reasons CWs do not adequately remove nitrogen from wastewater effluent, especially in temperate climates. First, design criteria for nitrogen removal are scarce for constructed wetlands. Second, as with all biological processes, dramatic changes in temperature, pH, dissolved oxygen (DO) and other factors can have a significant effect on nutrient removal rates. Low dissolved oxygen levels are a problem during the summer months (Brown and Reed, 1994; Crites *et al.*, 1997; White, 1995) and low temperatures are a problem during the winter (Crites *et al.*, 1997). Dissolved oxygen may also be a limiting factor during cold weather (Kemp and George, 1997; Mæhlum *et al.*, 1995). In the winter, ice formation restricts oxygen transfer, and studies have shown that vegetation doesn't provide oxygen after senescence (Mæhlum *et al.*, 1995). The problems associated with CWs located in colder climates have a particularly significant impact on nitrogen removal.

1.2.3 Nitrogen Removal Nitrification Limited

The mechanisms for ammonia removal in CWs include nitrification, plant uptake, and volatilization (Crites *et al.*, 1997). Of these three, ammonia removal in CWs is attributed primarily to nitrification (Crites *et al.*, 1997; Gale *et al.*, 1993; Bavor *et al.*, 1995). Nitrification is the most temperature sensitive process of all biological nutrient removal processes (Oleszkiewicz and Danesh, 1996); and nitrification is the limiting step in determining the nitrogen removal efficiency (Shammas, 1986). Constructed wetland studies by several researchers have concluded that during the winter season, nitrification is the controlling process in nitrogen removal (Hosomi, *et al*, 1994; Brown and Reed, 1994; Wittgren and Tobiason, 1995; Brix, 1987). Therefore, enhancing nitrification in a CW system appears to be the most important issue in nitrogen removal, especially from a regulatory standpoint.

1.2.4 Regulatory Impact of Poor Nitrification in CWs

The Indiana Department of Environmental Management (IDEM) and the Indiana State Department of Health (ISDH) are so concerned about the nitrogen removal problem that they issued a non-rule policy document in 1997 entitled "Constructed Wetland Wastewater Treatment Facilities Guidance"; their major concern is the constructed wetland's ability to nitrify ammonia and denitrify nitrate to nitrogen gas (IDEM, 1997). They conclude, from a review of discharge data and literature, that a constructed wetland without additional nitrogen removal treatment technologies may result in significant concentrations of ammonia in the effluent. Mæhlum *et al.* (1995) concluded that widespread application of CWs in Norway is not recommended until more knowledge on the nutrient purification processes in cold climates is known. Inadequate ammonia removal in CWs can have a significant impact on the environment.

1.2.5 Environmental Impact of Poor Nitrification

High effluent ammonia concentrations pose a problem for receiving water bodies. Effluents with a high ammonium concentration can cause many environmental problems. One problem is that ammonia degradation is an aerobic process that requires about 4.57 g O_2/g N oxidized. Low dissolved oxygen levels, caused by nitrification, can ultimately result in anoxic conditions and fish kills. Ammonia is extremely toxic to aquatic life; chronic concentrations as low as 0.0017 mg NH_3/L of undissociated ammonia have shown detrimental effects on freshwater fish (USEPA, 1986). Ammonia also contributes to the eutrophication of lakes and reservoirs.

CHAPTER 2
LITERATURE REVIEW

This review covers three topics important to this study: nitrification, constructed wetlands, and clinoptilolite. Nitrifying bacteria play an important role in the biological regeneration of ammonium-sorbed clinoptilolite. It is important to understand the environmental limitations of these bacteria, and how these limitations effect this study.

The second part of this chapter provides a substantial amount of background on constructed wetlands, how and why they were designed, and the shortfalls with their design and operation. The idea to develop the clinoptilolite system was based on the shortfalls of constructed wetland systems and the operational considerations used to overcome these shortfalls. Positive aspects of CW systems were used to develop the idea of a ion-exchange system based on a zeolite, clinoptilolite.

The final section of this chapter covers the physical attributes of clinoptilolite, and how its ion-exchange properties can be used to enhance nitrification in constructed wetlands through biological regeneration. Several previous studies that are related to this subject are discussed in this section.

2.1 Nitrification

2.1.1 The Nitrification Process

Nitrification is an important part of the nitrogen cycle. Nitrification is a two step process where ammonia is oxidized to nitrate. Chemo-litho-trophic nitrifying bacteria are considered to be the most important group of bacteria in the oxidation of ammonia (Laanbroek and Woldendorp, 1995). *Nitrosomonas* and *Nitrobacter* are the

chemolithic bacteria that are largely responsible for nitrification. Both *Nitrosomonas* and *Nitrobacter* are obligate aerobic, autotrophic bacteria. They use inorganic carbon (CO_2) as their electron donor and inorganic nitrogen as their electron acceptor.

Two main steps comprise the nitrification process; ammonium (NH_4^+) or ammonia (NH_3) is converted to nitrite (NO_2^-) by *Nitrosomonas* and nitrite is oxidized to nitrate (NO_3^-) by *Nitrobacter.* Nitrite production is a two-step process involving hydroxyl amine (NH_2OH) as an intermediate (Wood, 1986). No intermediate steps have been shown for the oxidation of nitrite (Wood, 1986). The growth of *Nitrosomonas* is considered the limiting step in the overall nitrification process (Antoniou *et al.*, 1990).

In the environmental engineering field, nitrification is typically represented by the following chemical equations:

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + 2H^+ + H_2O \qquad \textbf{(2.1)}$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^- \qquad \textbf{(2.2)}$$

However, most researchers today agree that ammonia is the primary substrate (Suzuki *et al.*, 1974; Wood, 1986; Shammas, 1986). It is apparent that the oxidation of ammonium requires oxygen and produces protons. Stochiometrically, 4.57 grams of oxygen is consumed per gram of ammonium nitrogen that is nitrified, and 7.14 grams of alkalinity as calcium carbonate ($CaCO_3$) is consumed per gram NH_4N oxidized. Besides substrate availability, there are other factors that limit reaction kinetics.

2.1.2 Kinetics - Limitations to Nitrification

Three important factors that influence nitrification rates are dissolved oxygen (DO), pH and temperature. As shown earlier, oxygen is required for the oxidation of ammonia. The pH plays an important role in the availability of the ammonia while temperature also affects the availability of ammonia and oxygen. Suboptimal temperatures can inhibit the nitrifiers and it also plays an important role in the "population shift" capabilities of the nitrifying community. The presence of an

attachment site for nitrifying bacteria affects how well the nitrifiers respond to changes in these parameters.

2.1.2.1 Dissolve Oxygen (DO)

Since nitrifying bacteria are strict aerobes the DO concentration is an important consideration. There is a minimum DO concentration below which nitrifiers will not function, but there is no real consensus as to what that concentration is. Randall and Buth (1994) state that DO levels above 2 mg/L are adequate for nitrification. Wild *et al.* (1971) concludes that any DO concentration above 1 mg/L is adequate for nitrification to occur. However, neither of these authors investigated what effect, if any, that DO has on nitrification kinetics above the minimum concentration that they cited.

Semmens *et al.* (1977b) showed that the nitrification rate is inhibited at any DO concentration lower than 6 mg/L. The Semmens study showed that the nitrification rate dropped to 33 percent of its maximum value at 2 mg/L. Therefore, the availability of DO is an extremely important consideration in nitrification kinetics. However, the main issue in designing a nitrifying system is the ability to supply the minimum level required to oxidize ammonia.

2.1.2.2 pH

pH is also an important consideration in nitrification kinetics because NH_3, as discussed earlier, is the preferred substrate by *Nitrosomonas* for nitrite production. There is no universal consensus on the optimal pH for nitrification. Antoniou *et al.* (1990) conducted an extensive literature review and reported an optimal pH range of 7.0 - 8.2. Other researchers differ; Shammas (1986) reported an optimal pH for nitrification in the range of 8 - 9. Painter and Loveless (1983) found the optimum pH to be 7.5 to 8.0 for most of their experiments with activated sludge. They reported 6.2 as the minimum pH below which nitrification would not occur.

The optimal pH also differs between *Nitrosomonas* and *Nitrobacter*. The optimal pH for ammonia oxidation by *Nitrosomonas* is reported as 6.8 to 9.0, and 6.7 to

9.0 by Engel and Alexander (1958), and Groeneweg *et al.* (1994) respectively, but Groeneweg noted that the optimal oxidation pH may not be the same as the optimal growth pH for *Nitrosomonas*. Comparing the pH values for the overall nitrification process with the pH values for ammonia oxidation it appears that *Nitrobacter* may be more limited by low pH than *Nitrosomonas*.

Since ammonia is a base, pH also effects the substrate availability of ammonia, and in turn temperature affects the dissociation constant of ammonium. The dissociation constant, pK_a, for ammonium is 9.25 at 25°C. Temperature dependence is given by:

$$pK_a = 0.09018 + \frac{2729.92}{T_a} \qquad \textbf{(2.3)}$$

Where pK_a is the log of the dissociation constant and T_a is the absolute temperature (°K) (Chapra, 1997).

As the temperature decreases the pK_a increases, and the NH_3 availability decreases. A general trend shows that as the pH decreases in a waste stream the rate of nitrification decreases (Shammas, 1986). Therefore, colder temperatures could reduce nitrification by *Nitrosomonas* just by reducing the overall NH_3 availability. However, Groeneweg *et al.* (1994) found that temperature has a much stronger effect on the rate of ammonia oxidation than the temperature dependent shift in NH_3 availability. So even though adequate ammonia substrate is available, the nitrifiers are limited in their ability to oxidize the ammonia at the lower temperatures.

2.1.2.3 Temperature

Nitrification is generally considered to be the most temperature-sensitive process in biological nutrient removal (Oleszkiewicz and Danesh, 1996). It is generally agreed upon that optimal nitrification occurs at approximately 30°C - 35°C (Shammas, 1986; Hammer and Knight, 1994). Charley *et al.* (1980) reported that the optimal

temperature for ammonia oxidation to nitrite is around 15°C. *Nitrobacter* may be influenced by lower temperatures more than *Nitrosomonas*.

As with pH, there is no consensus as to the lowest temperature where nitrification ceases. Literature values range from 2°C to 18°C (Oleszkiewicz and Berquist, 1988; Hammer and Knight, 1994; Crites, 1994; Groeneweg *et al.*, 1994; Kemp and George, 1997). As with any biological microorganism, as the temperature decreases the generation time increases, or the bacterial growth rate decreases. Generation times for nitrifying bacteria range from 150-200 hours at 5°C to 15 hours at 30°C. (Wijffels *et al.*, 1995)

A modified Arrhenius equation can be used to show the relationship between temperature and the nitrification rate.

$$k_T = k_{20}\, e^{b(T-20)} \qquad \textbf{(2.4)}$$

Where k_T is the maximum rate constant at temperature T (1/d); k_{20} is the maximum rate constant at temperature 20°C (1/d); T is temperature (°C); and b is the temperature coefficient. Another way to write the same equation is:

$$k_T = k_{20}\, \theta^{(T-20)} \qquad \textbf{(2.5)}$$

Where θ is the temperature correction factor.

Shammas (1986) did an extensive literature review of temperature coefficients (b), two values are important for wetlands systems. Those obtained by Knowles *et al.* (1965) for Thames estuary water and Stratton and McCarthy (1967) for river water should most closely approximate wetland conditions (Table 2.1). The coefficients are equivalent to temperature correction factors, θ, of 1.10, 1.06, 1.09, and 1.06 which are similar to values found in literature. Oleszkiewicz and Berquist (1988) conducted a cold temperature nitrification study and reported that the temperature correction factor increases significantly as the temperature decreases below 7°C, meaning that even though nitrification is still occurring at low temperatures, it decreases dramatically below 7°C. Using the data from Table 2.1, it is important to note that the

Table 2.1: Temperature coefficients for the maximum nitrification rate constants (Adapted from Shammas, 1986).

Temperature Coefficient	Conditions
	Thames estuary water
0.095	Ammonia to nitrite
0.059	Nitrite to nitrate
	River water
0.084	Ammonia to nitrite
0.056	Nitrite to nitrate

temperature coefficient for *Nitrobacter* is smaller than that for *Nitrosomonas*. Therefore, temperature has a greater effect on nitrate formation than on nitrite formation; and there exists a critical temperature below which nitrite formation will exceed nitrate formation (Randall and Buth, 1984). In either case, there is a temperature at which both nitrite and nitrate production will cease.

2.1.2.4 Population Shift in Nitrifying Bacteria

One reason BOD reduction does not suffer as much in colder climates is that heterotrophic bacteria can compensate for declining temperatures with a population shift. Psychrophilic bacteria replace mesophilic bacteria, and organic compounds are continually oxidized. However, nitrifying bacteria cannot compensate with a population shift, because the nitrifying bacteria that are responsible for nitrification at mesophilic temperatures are typically the same bacteria that perform nitrification at psychrophilic temperatures, so that as the temperature decreases the growth rate and oxidation rate also decrease.

2.1.2.5 Importance of Bacterial Attachment

The highest populations of nitrifying bacteria occur as layered growths on attached substrates; only rarely do they occur as free floating forms (Hammer and Knight, 1994). Nitrifiers are less sensitive to temperatures when the bacteria are immobilized (Wijffels *et al.*, 1995). Therefore, processes that incorporate some type of media for

biomass attachment should be more effective than processes that do not use some type of biomass attachment media. Constructed wetlands utilize this concept for waste treatment.

2.2 Constructed Wetlands

Constructed wetlands are becoming more prevalent in the United States as a biological, chemical and physical treatment process. Current applications include primary settled and secondary treatment sewage, tertiary effluent polishing, disinfection, urban and rural run-off management, toxicant management, land-fill and mining leachate treatment, sludge management, industrial effluent treatment, enhancement of in stream nutrient assimilation, nutrient removal via biomass production and export, and groundwater recharge (Bavor *et al.*, 1995). Table 2.2 outlines the advantages and disadvantages of a constructed wetland treatment system compared to other conventional treatment processes.

There are two main types of constructed wetlands built in the United States: surface flow wetland (SFW) and subsurface flow wetland (SSF) (Brown and Reed, 1994; Crites, 1994). There are several variations to these two types of CWs, but the basic design is still the same. In fact, most systems are a combination of the two incorporating facultative lagoons (~ 42 %), septic tanks (24 %), and other treatment processes (Brown and Reed, 1994).

Table 2.2: Constructed wetland advantages and disadvantages. (Luise, 1994; Brix 1987, Bavor *et al.*, 1995)

Advantages	Disadvantages
➜ low capital and maintenance costs ➜ low energy requirements ➜ low maintenance requirements; don't require vast technical expertise to operate ➜ they can be built at the very location where the WW is produced ➜ water quality improvement ➜ suitable for treating wastewater associated with non-point source pollution ➜ flood storage and the desynchronization of storm rainfall and surface runoff ➜ cycling of nutrients and other materials ➜ habitat for fish and wildlife ➜ passive recreation, such as bird watching and photography ➜ active recreation, such as hunting	➜ generally require larger land areas than do conventional treatment processes ➜ performance may be less consistent than in conventional treatment processes ➜ biological components are sensitive to toxic chemicals ➜ flushes of pollutants or surges in water flow may reduce treatment efficiencies ➜ they require a minimum amount of water if they are to survive

2.2.1 Constructed Wetland Types

2.2.1.1 Surface Flow Wetlands (SFW)

Surface flow wetlands are also called free-water surface wetlands. A SFW (Figure 2.1) is designed so that the water surface is above the ground level. A liner is be placed over the native soil to help retain water and prevent groundwater contamination. Soil is placed over the liner to provide a media for emergent vegetation growth. A majority of the treatment is considered to take place in the free water of the wetland. The top layer of water is oxic while the lower layers of water and sediments are normally anoxic. Detention time, organic loading rate, water depth, aspect ratio, mosquito control, and vegetation harvesting are all important design criteria (Crites, 1994). An advantage of SFWs are that they provide more biologically diverse ancillary benefits than subsurface flow wetlands (Kadlec, 1995). Two disadvantages are that mosquito production and algal growth can be a problem. Design criteria for a SFW are summarized in Table 2.3.

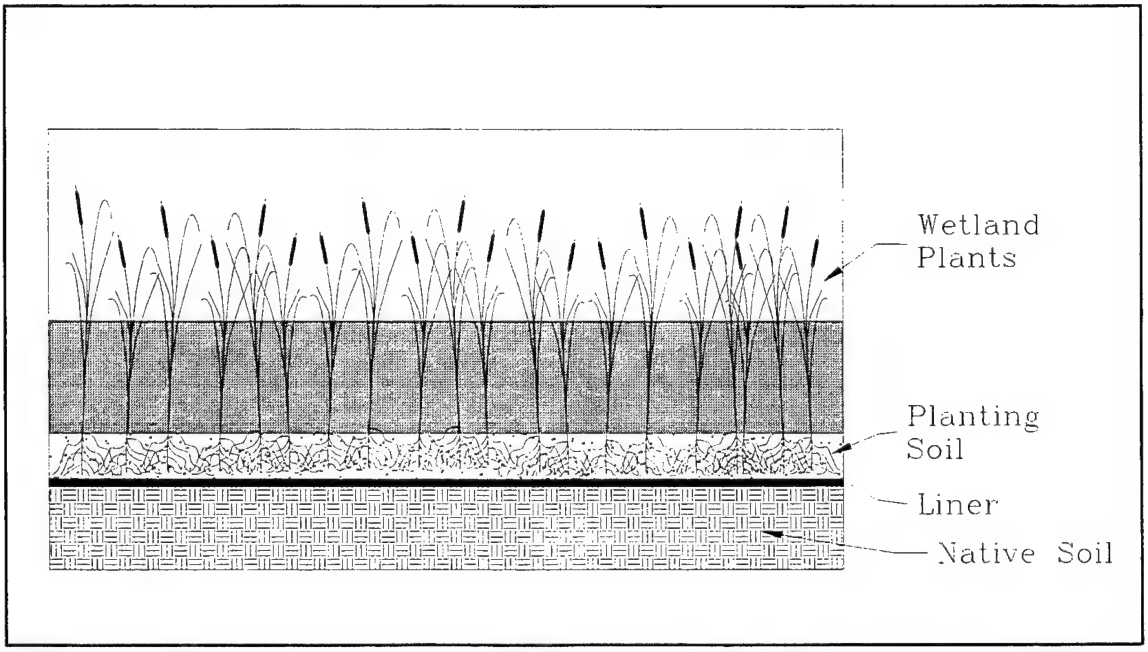

Figure 2.1: Surface flow constructed wetland.

Table 2.3: Typical design criteria for SFW. Design equations vary among researchers and should be checked before using design values.

Factor	**Typical value**
Detention time, d	5 – 14 (8 – 14 for N removal) (Crites, 1994) 4 – 15 (Tchobanoglous and Burton, 1991)
Maximum BOD5 loading rate, kg/ha/d	80 (Crites, 1994) 100 (Reed and Brown, 1995) 11 (Tchobanoglous and Burton, 1991)
Total nitrogen loading rate, kg/ha/d	3 – 5 (Hammer and Knight, 1994)
Water depth, m	0.1 – 0.5 (Crites, 1994) 0.05 – 0.9, 0.3 –0.45 typical (Brown and Reed, 1994) 0.1 – 0.6 (Tchobanoglous and Burton, 1991)
Hydraulic loading rate, mm/d	7 – 60 (Crites, 1994) 20-30 (Hammer and Knight, 1994) 140 – 468 (Tchobanoglous and Burton, 1991)
Area requirement, $ha/m^3/d$	0.002 – 0.014 (Crites, 1994)
Aspect ratio, L:W	2:1 – 10:1 (Crites, 1994)
Mosquito control	Required (Crites, 1994)
Harvest frequency, yr	3 – 5 (Crites, 1994)

2.2.1.2 Subsurface Flow Wetlands (SSF)

Other names for SSF wetlands are reed beds, or root zone method. The water level is below ground surface in a SSF wetland (Figure 2.2). A liner serves the same purpose as it does for a SFW, but the soil media is normally porous to allow for water flow through the media. The vegetation is an important part of the SSF design. The root zone, or rhizome, provides aerobic conditions, while the remaining portion of the SSF is

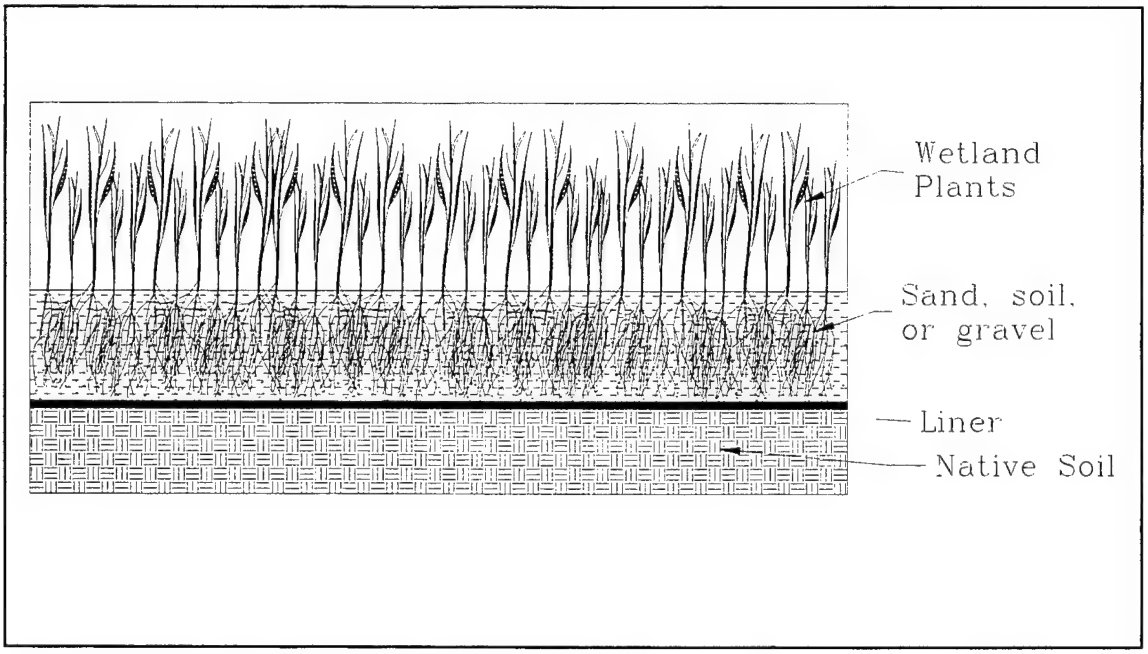

Figure 2.2: Subsurface flow constructed wetland.

anaerobic. The rhizosphere increases and stabilizes the hydraulic conductivity of the soil (Brix, 1987). Detention time, BOD, solids loading rate, media depth and size, and subsurface hydraulics are important design criteria for the SSF wetland (Crites, 1994). Mæhlum *et al.* (1995) includes characteristics of applied wastewater, filter medium, depth of liquid in the system, detention time, control of flow path, type of vegetation, and vegetation management as important design variables for designing a SSF wetland.

One of the biggest disadvantages of SSF wetlands is the cost of the media. Advantages over SFW include: algae production is limited, mosquitoes are not a problem, better thermal protection, attachment sites are more stable, and microbial biomass concentrations are greater (Wood, 1995). These advantages can result an overall smaller wetland size when compared to a SFW. Design criteria for a SSF wetland are summarized in Table 2.4.

Table 2.4: Typical design criteria for SSF wetland. Design equations vary among researchers and should be checked before using design values.

Factor	**Typical value**
Detention time, d	2 – 7 (Crites, 1994) 4 – 15 (Tchobanoglous and Burton, 1991)
Media depth, mm	0.1 – 0.75 (Crites, 1994) 0.2 – 0.76 (Brown and Reed, 1994; Tchobanoglous and Burton, 1991) < 0.62 (USEPA, 1993)
Media size, mm	5 – 230, 13 – 76 typical (Crites, 1994) 6 – 130, 13 – 80 typical (Brown and Reed, 1994) 12.7 – 25.4 (USEPA, 1993)
Maximum BOD5 loading rate, kg/ha/d	75 (Crites, 1994) 100 (Reed and Brown, 1995) 11 (Tchobanoglous and Burton, 1991)
Hydraulic loading rate, mm/d	140 – 468 (Tchobanoglous and Burton, 1991) 38 – 55 (Yin and Shen, 1995) 15 (for N removal) (Platzer and Netter, 1994)
Bottom slope, %	0 – 2 (Crites, 1994) 0 – 1 (Brown and Reed, 1994)
Aspect ratio, L:W	< 1:1 (Crites, 1994) < 2:1 (USEPA, 1993)

2.2.2 Wetland Plants

The wetland plants that are used in a constructed wetland design are an important consideration. The plants must be more than aesthetically pleasing. Plant diversity is not necessarily an important issue. The main objective of constructed wetlands is to treat various types of waste streams. This objective may be easily met with a single monoculture that can flourish in the waste stream. In fact, most CWs are built using monocultures of bulrushes, cattails, or reeds.

Plant selection should be based upon the conditions caused by the waste stream, but the plant functionality is also an important consideration and is discussed further in this section. Plant type can also influence nitrogen uptake, and some researchers and engineers recommend plant harvests as a method of enhancing nitrogen removal in constructed wetlands. This is also discussed in this chapter.

2.2.2.1 Common Types

Some plants commonly used in SFWs are *Typha* ssp. (cattails) and *Scirpus* ssp. (bulrushes), while the common reed, *Phragmites australis*, is mainly used in SSF wetlands (Kadlec, 1995). *Phragmites* is preferred because it has a dense rhizome structure, that typically penetrates deep into the soil matrix (Brix, 1987). IDEM (1997) has banned *Phragmites* from use in Indiana because they proliferate so well and takeover and significantly alter the diversity of nearby natural wetlands.

2.2.2.2 Plant Function and Adaptation

Wetland plants are important to both types of wetland systems, though some investigators have found that plant presence has no statistical significance (Kemp and George, 1997). However, the purpose of plants is different between the two types of wetland systems. In SFW the plant shoots provide attachment sites for bacteria. Bacterial attachment sites increase as plant density increases. In SSF, the root or rhizome provides an attachment site for bacteria, and they also provide oxygen for the bacteria through their root structures. Wetland plants are morphologically adapted to grow in a

water saturated sediment by virtue of large internal air spaces for the transportation of oxygen to the roots and rhizomes (Brix, 1994). The oxygen that leaks from the roots creates an oxidizing zone within the anoxic substrate and stimulates both aerobic decomposition of organic matter and growth of nitrifying bacteria (Brix, 1994). Some researchers feel that aeration is provided in a limited capacity for nitrification (Reed and Brown, 1995). Plants can also remove nitrogen and store it as biomass.

2.2.2.3 Nutrient Uptake

Nutrients removed by plants do not contribute to overall nutrient removal unless the plants are harvested. Literature values differ on the impact that plant uptake has on nitrogen removal due to plant harvesting. Brix (1987) says that nutrients taken up during one growing season constitute only a few percent of the total contents introduced into the wetland. Herskowitz (1986) determined that less than 10 % of the influent nitrogen was removed by plant harvesting. Koottatep and Polprasert (1997) found that plant uptake amounted to about 43 % of the total influent nitrogen in a SFW constructed wetland operating at a hydraulic retention time of 5 days. The number of plant harvests conducted annually also plays an important role in the overall nutrient removal. More nutrients can be removed as the number of plant harvests increases. However, as the number of plant harvests increase the cost also increases.

A better, and more general measure of the nutrient removal capacity for wetland plants is the nutrient mass removed normalized to wetland area. The uptake capacity of emergent macrophytes is approximately 1000 - 2500 kg N/ha/yr (Brix, 1994). Wittgren and Mæhlum (1997) summarized nutrient uptake for various plant species in cold temperate climates. Uptake values ranged from 107 - 434 kg/ha/yr. Drizo *et al.* (1997) reported nitrogen uptake in *Phragmites australis* as 640 kg/ha/yr for the above ground biomass. Koottatep and Polprasert (1997) reported the highest values of 2690 - 2740 kg/ha/yr (tropical conditions).

Most uptake occurs in the root and rhizome structure (Hiley, 1995). Therefore, harvesting stem and leaf biomass will only remove a small portion of the

nitrogen and the rest will be recycled as the roots and rhizomes mineralize. Because of this effluent ammonium concentrations will always be about 0.9 mg N/L, because of plant degradation (Cooper *et al.*, 1997). This is because when the vegetation dies a portion of the organic nitrogen is eventually converted to ammonium as part of the nitrogen cycle; but even when plants are decaying they play an important role in the nitrogen removal in CWs. They serve as a carbon source for denitrification in CWs (Kemp and George, 1997), deleting the requirement to augment CW systems with methanol.

Overall, the impact of cold temperatures on nitrification outweighs the benefits gained by plant harvests. In fact, in cold climates with inhibited nitrification there can be a net production in ammonium where the effluent concentration exceeds the influent concentration. To make matters worse, the decomposing plant detritus can also result in an effluent BOD concentration in the range of 2 to 7 mg/L (Reed and Brown, 1995).

Poor nitrification cannot be blamed completely on the cold temperatures. Root zone development in the SSF treatment zone is extremely important for proper wetland functioning. Reed and Brown (1995) found that root/rhizome penetration in most SSF systems is limited to about 0.3 m regardless of the plant species. Based on the range of the designed media depth for a SSF wetland, over half of the media has no root penetration which could result in anoxic conditions in the bottom portions of the cell, and poor nitrogen removal efficiencies.

2.2.3 Wetland Media

2.2.3.1 Function of Wetland Media

The soil media used to build a SSF CW system is also extremely important. It provides a stable surface area for microbial attachment, a solid substrate for plant growth, and functions directly in the purification of the wastewater by the way of physical and chemical processes (Brix, 1987). Soils with high cation-exchange capacities

(CEC), like clays or organic soils, play an important role in nutrient removal, and even enhance nitrification (Platzer and Netter, 1994; Mæhlum *et al.*, 1995). CWs with higher nitrogen removal efficiencies were typically SSF systems with some type of media that retarded the migration of ammonium through the wetland, and is one of the main reasons that a clinoptilolite based treatment system was investigated in this study.

Brix (1987) found that the adsorption of ammonia to the soil matrix probably the main mechanism of nitrogen removal. Charged nutrients, like NH_4^+, adsorb to the charged soil particles which acts as a retardation factor increasing the detention time of the ion. However, Gale *et al.* (1993) found that nitrogen removal was more rapid in wetlands with mineral soils than organic soils. Coarse soils, like gravel, do not typically have a high CEC, but Drizo *et al.* (1997) were able to completely remove all ammonia, and 85 – 95 % of the nitrate using shale as a soil media in a SSF wetland system.

Coarse soils are also important for the hydraulic conductivities needed to ensure short-circuiting does not occur in the SSF wetland system. Poor hydraulic design is the number one cause of wetland system failure (Reed and Brown, 1995).

2.2.4 Constructed Wetland Design Shortfalls

There are two main reasons that CWs are not very efficient at removing nitrogen from a municipal waste stream. First, there is no reliable design consensus. Second, most of the current designs are based upon BOD removal, when in fact, nitrogen is typically the limiting design parameter. In some areas, systems may be working well, but engineers and regulators disregard the effect that evapotranspiration (ET) has on the efficiency of the CW by considering effluent concentration only and not the total mass discharged. There are many different strategies for overcoming these shortfalls, but none that directly assesses the nitrogen (ammonium) removal problem.

2.2.4.1 Limited Operational System Database

There is no design consensus for constructed wetland systems (Wood, 1995). A wetlands inventory study concluded that constructed wetland design approaches appeared to range from trial and error to semi- empirical to semi-rational using design models based on very limited data (Brown and Reed, 1994). This is because original designs were based upon a limited database, the North American Wetland Treatment System Database (NAWTD).

The NAWTD, was developed with support from the EPA's Wetlands Research Program, and was assimilating data from operational CW systems so fast that existing design criteria were quickly outdated by new empirical results (Knight, 1994). This would make most designs obsolete. Funding for the database has ceased and there is no current move to update the database (D. Brown, USEPA), but the information gathered so far is inadequate to develop an all-encompassing CW design.

Kaldec (1995), concludes that regression equations derived from the database are of limited use because they embed too many site specific parameters. Bavor *et al.* (1995) agrees that current models are too system specific, but states that the real problem is that the key process mechanisms of CW treatment are still poorly understood. As a result, there is still no consensus on system configuration and design, and the future appears bleak. The nuances of each situation preclude a "cookbook" approach to design (Kadlec, 1995), and cannot ensure an effective design that will adequately remove nitrogen.

2.2.4.2 Poor Nutrient (Nitrogen) Removal

Ammonia removal in most of the present generation of operating SSF systems in the U.S. is deficient (Reed and Brown, 1995). Both types of constructed wetlands are effective at removing BOD, TSS, and bacteria, however, these systems do not typically meet NH_3N effluent limits of 2-6 mg/L (Brown and Reed, 1994). The situation is worse as the ambient temperature decreases. BOD and TSS removal continues to be quite good during the winter months, while NH_3 removal remains

inefficient (Brown and Reed, 1994). Inadequate nitrogen removal will drive future designs. Future constructed wetlands will likely be designed for nutrient removal, with BOD, TSS and bacteria removal as secondary objectives (Hammer and Knight, 1994). IDEM's stance on CWs is a testament to this statement.

2.2.4.2.1 Reasons for Poor Removal

Many reasons have been cited for the poor nutrient removal efficiencies of wetland systems. Some reasons include: inadequate detention times, poor oxygen transfer, ammonium release from the sediments, and a lack of suitable ion-exchange sites. These reasons may not be directly responsible for the low temperature nitrogen removal deficiencies, but may contribute indirectly. Detention time and oxygen transfer can limit nitrification and subsequent nitrogen removal in SSF wetlands (Crites, 1994). During the winter months longer detention times are necessary for the slower nitrification kinetics. In the winter months, ice layers can restrict aeration, affecting the DO availability for nitrifying bacteria (Yin and Shen, 1995). Ammonium is continually released from bottom sediments during the winter (Hosomi *et al.,* 1994). Plant detritus plays an important role in this. Finally, a lack of suitable surfaces for ion-exchange of NH_4^+, as well as attachment for nitrifiers are considered potentially limiting factors for nitrification in CWs (Wittgren and Tobiason, 1995).

2.2.4.1.2 Evapotranspiration

ET is important from a regulatory and mass-balance perspective. It plays a significant role in wetland efficiency and yet its impact is not well understood or researched. In one study, three horizontal reed beds located in Germany were evaluated for nitrogen removal. ET was found to be one of the strongest factors supporting nitrification (Platzer and Netter, 1994). When ET is significant, removal efficiency should be evaluated on a mass-removal basis. Mark Harrison, a design engineer for J.F. New and Associates stated that based on a mass loading basis, better than 90% reduction in nitrogen removal occurs due to ET. In the future, ET may be an important consideration for permitting constructed wetlands.

2.2.5 Overcoming the Constructed Wetland Design Shortfalls

It is important to understand the implications of the design shortfalls and develop a strategy to overcome these shortfalls, especially in temperate areas where the shortfall may be intensified.

2.2.5.1 Understanding Shortcomings and Applying Simple Strategies

As discussed earlier, moderate to high nitrification rates required moderate temperature and pH conditions, microbial attachment substrates, and adequate supplies of oxygen (Hammer and Knight, 1994). The overall effect of the lower temperatures are slower growth rates and nitrification kinetics. The hydraulic loading rate and/or solids loading rate can be adjusted to compensate for this shortfall (Yin and Shen, 1995). Both the hydraulic loading rate and solids loading rate can be reduced. However, there is no consensus as to which factor is more important and has a more significant impact on enhancing the nitrogen removal efficiency.

Hammer and Knight (1994) found that efficient nitrification can be achieved by using loading rates of less than 3 kg N/ha/d, providing alternating aerobic (pond) and anaerobic (marsh) zones are present in the wetland system. Even though most wetland designs use mass loading rate to design their systems, Platzer and Netter (1994) concluded that hydraulic loading is more important than mass loading and recommend a loading of less than 15 mm/d to guarantee high nitrogen removal. Other authors disagree, and loading rates vary significantly. Yin and Shen (1995) recommend a hydraulic loading rate of 38-55 mm/d (TN < 15 mg/L) for a study conducted with average ambient temperatures of less than -4°C. White (1995) recommended a hydraulic loading rate of less than 17 mm/d for a single-stage wetland, and 36 mm/d for a two-stage (unsaturated inlet zone, and recirculation) system. However, temperature was not a controlling factor in determining the hydraulic loading rate in White's design. All data were collected for temperatures greater than 15°C.

No matter which factor is considered to be the most important, BOD removal in the first stages of a multi-stage wetland system is essential to enhancing nitrification (White, 1995). This assures that adequate DO is available for nitrification.

If ice-layers interfere with aeration this alone may not alleviate the nitrogen removal problem. DO availability can be increased with aerobic pretreatment (Mæhlum, *et al.*, 1995). All of these design considerations may increase nitrification efficiency, but none of them can alleviate the problems caused by cold temperatures on nitrification kinetics.

2.2.5.2 Design Solutions to Enhance Nitrification

One of the most straight forward solutions to overcoming low winter nitrification rates is to design a storage system for all incoming waste during the winter months. A Minot, ND wastewater-wetland treatment system stores the wastewater generated by 35,000 people for 180 days. (Hammer and Knight, 1994) All treatment takes place during the growing season in a marsh-pond-marsh wetland system and the system meets an effluent discharge limit of 1 mg NH_4N/ L. The advantage of this approach is that warm weather design parameters are readily available (Wittgren and Mæhlum, 1997), and the fact that the CW will be smaller because optimal, summer conditions are used for the design. Also, the loading rate can be controlled. However, even though the storage system is easily designed it requires a lot of land, which may not be available, or is very costly.

One recommendation for improving nitrogen removal requires the combinations of aerobic and anaerobic environments that can be provided by alternating water depths and appropriate combinations of wetland vegetation (Hammer and Knight, 1994). Another recommendation is to use different variations of vertical flow SSF wetlands. These types of CWs are typically found in Europe and may be better suited to remove nutrients (Laber *et al.*, 1997; Morris and Herber, 1997; Cooper *et al.*, 1997). The vertical flow systems are modeled after trickling filters. Intermittent filling and emptying can be used in conjunction with the vertical flow units and may be a more efficient regime that will optimize both nitrification and denitrification (Wittgren and Tobiason, 1995). Reciprocating rock biofilters (RRB) developed by Tennessee Valley Authority scientists takes advantage of this important concept.

In a RRB, two subsurface flow wetlands are alternately drained and filled, which cycles the wetland between aerobic and anaerobic processes respectively. The

process operates much like a mechanical trickling filter. Oxygen diffusion increases by as much as 400% during the drain cycle and ammonia is reduced to undetectable levels (Kratch, 1996). The RRB may have limited applications in extremely cold climates where the rock media would freeze during the drain cycle. Green *et al.* (1998) investigated a similar system in the laboratory that uses passive aeration to enhance nitrification by increasing available oxygen in the soil substrate. They were able to obtain an average nitrification efficiency of 96%.

2.3 Clinoptilolite

One alternative to either of these systems is to chemically store the ammonium during the colder winter months using an ion-exchange media, and biologically regenerating the media during the warmer summer months when conditions are more conducive for nitrification. Clinoptilolite, a zeolite, has many physical properties which make it an excellent candidate for such a system. This system was tested in this study.

2.3.1 Clinoptilolite - The Media

Clinoptilolite is the most abundant and commonly used zeolite material (Allen, 1997) . More than 95% of the natural zeolites produced in the United States are clinoptilolite, and the largest producers of clinoptilolite are St. Cloud Mining (Winston, NM), Zeotech (Tilden, TX), and Teague Mineral Products (Adrian, OR) (Eyde, 1995). Zeolites are formed from volcanic sediment under conditions of high pH and in the presence of aluminum and silicon .

Zeolites look much like a grain of sand, and typically contain sodium, silicon, aluminum and oxygen (Figure 2.3). The atoms of aluminum, silicon, and oxygen are bonded into a vast anionic network similar in structure to such macromolecular solids as quartz . Clinoptilolite is one of 40 different types of mined zeolites, and has a Si/Al ratio of approximately 5:1 (Czárán *et al.*, 1988). Clinoptilolite is an open zeolite comprised of channels, pores and ion cages or cavities (Koon and Kaufman, 1971). Channels are the passages and restrictions between exchange sites in the zeolite. Pores

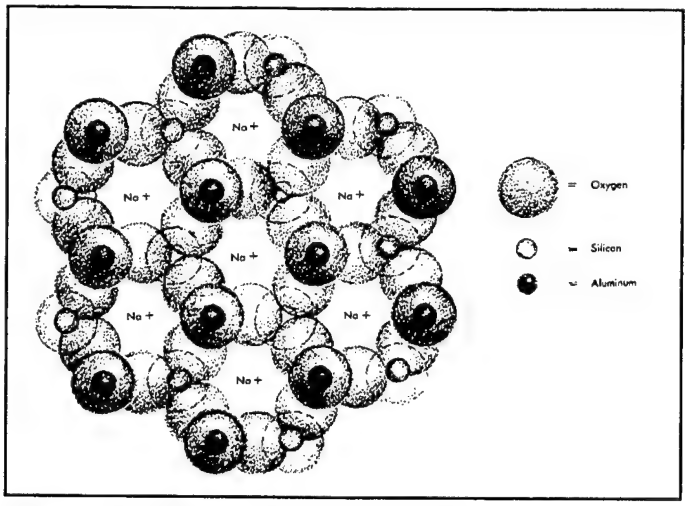

Figure 2.3: Clinoptilolite structure.

(intra crystalline) are openings between the same zeolite crystals, but within the same aggregate. Ion cages or cavities are the enlargements that contain the exchange sites. Interpartcle pores are pores between aggregates of zeolite crystallites.

Within the cages a large portion of Al^{3+} substitutes for Si^{4+} resulting in the negative charge of the network, and high CEC (Huang and Petrovic, 1994). The negative charge of the network is compensated for by a large number of Na^+ or K^+ ions located in the cages within the atomic lattice. Nothing happens if pure water is passed though a zeolite column. The crystals themselves contain far too many atoms to dissolve in water and the small Na^+ or K^+ ions cannot dissolve since this would leave behind an unstable anionic network carrying a large negative charge. However, if the water coming in contact with the zeolite contains exchangeable ions, the situation is quite different. Some of the positive ions in the water change positions with the sodium ions in the lattice.

Some ions will exchange more easily with the Na^+ or K^+ ions than others. The order of preference for various cations in decreasing order is $Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$ (Ames, 1960), $Pb > NH_4 > Cu, Cd > Zn, Co > Ni > Hg$ (Blanchard *et al.*, 1984), and as $K^+ > NH_4^+ > H^+ > Na^+ > Sr^{2+} > Ca^{2+} > Mg^{2+} > Li^+$ (Goto and Ninaki, 1980).

2.3.2 Clinoptilolite and Ion-Exchange

2.3.2.1 Exchange Capacity

The total ion-exchange capacity of clinoptilolite has been measured as 1.6 to 2.0 meq/g (USEPA, 1975). It is recommended that zeolite minerals should have a cation-exchange capacity of at least 1.25 meq/g to be used in most ion-exchange applications (Eyde, 1995). Bernal and Lopez-Real (1993) reported ion-exchange capacities of 8.149 to 15.169 mg N/g clinoptilolite (0.58 – 1.08 meq/g). The operating capacity for NH_4^+ ions in the presence of other cations found in domestic wastewaters is about 0.4 meq/g. Koon and Kaufman (1971) empirically related resin ammonium concentration to cationic strength, as cationic strength increased above 0.015 mol/L the total ammonium exchange capacity of the clinoptilolite decreased to about 0.2 meq/L. This number is not impressive compared to other synthetic ion-exchange resins, but the fact that clinoptilolite has a higher affinity for NH_4^+ than it does for Ca^{2+}, Mg^{2+}, and Na^+ is extremely important.

It is because of clinoptilolite's high affinity for NH_4^+ over other cations that it can be used as an ion-exchange resin for NH_4^+ removal. Ammonium does not attract as much water of hydration compared to the other cations, therefore it is freer to migrate through the lattice and closely approach exchange sites. Typical ion sizes are found in Table 2.5.

The extent to which cations can be exchanged depends on the nature of the zeolite cages, which is also a function of the Si/Al ratio in the zeolite framework. The hydrated cations must be able to migrate through the pores and channels to get to the cages. Barrer (1958) determined the minimum free diameter of zeolite channels as 2.2 – 9Å, while Ferguson and Pepper (1987) reported a pore size of 10^{-9} m. Channel and pore analysis has evolved significantly since the Barrer study, and Ackley and Yang (1991) provide an extensive look at the structure of clinoptilolite in their study. Unlike synthetic resins, clinoptilolite is unable to swell to accommodate the cation's larger hydrated radius. Therefore, none of the ions can enter the cages without some of the water of hydration being stripped from the ion (Koon and Kaufman, 1971).

Table 2.5: Crystal diameters and hydrated diameters of selected cations. (Koon and Kaufman, 1971 as reported in [a]Pauling, 1948; and [b]Grim 1968)

Ion	Crystal Diameter[a] (Å)	Hydrated Diameter[b] (Å)
Li	1.20	20.0
Na	1.90	15.8
K	2.66	10.6
NH4	2.80	10.7
Rb	2.96	10.2
Cs	3.38	10.1
Mg	1.30	21.6
Ca	1.98	19.2
Sr	2.26	19.2
Ba	2.70	17.6

2.3.2.2 Exchange Kinetics

Ammonium adsorption in clinoptilolite is a relatively quick process. Bernal and Lopez-Real (1993) found that ammonium adsorption was essentially complete after one hour of shaking in batch experiments, and particle size did not have any effect on the amount of ammonium adsorbed in the clinoptilolite. Haralambous *et al.* (1992) found that it took only ten minutes to reach 34.5 % of the ammonium equilibrium exchange capacity.

In the general form, ammonium ion-exchange in clinoptilolite can be represented by the following chemical equation:

$$S{:}NH_4^+ + A^+ \leftrightarrow S{:}A^+ + NH_4^+ \qquad \textbf{(2.6)}$$

Where S: represents the ion-exchange surface of the resin, and A^+ any monovalent cation. As ammonium is exchanged it becomes available in the free solution.

2.3.3 Regeneration

Clinoptilolite, like any ion-exchange resin, requires exchange ions to be regenerated. Typically, the ammonium is desorbed from the clinoptilolite by creating a chemical gradient with a high concentration of competing cations. The method is usually very effective, but disposing of the waste product can be a problem because of the high ammonium concentration. Benefield, *et al.* (1982) lists two possible alternatives to remove the ammonium from the regenerant. In the first process, a high pH regenerant, like a lime solution, is used to convert the ammonium to ammonia which can be air stripped. The exchange ion used in this case would be Ca^{2+}. Sulfuric acid is used in the second process. The acid is not used as the regenerant, but the spent regenerant is passed through the acid and ammonium sulfate is produced which can be sold as fertilizer. The chemical equation representing this process is:

$$2NH_4^+ + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H^+ \qquad \textbf{(2.7)}$$

The third possibility that is not mentioned by Benefield *et al.* (1982) is to use nitrifying bacteria to convert the ammonium in the regenerant to nitrate. This process is called biological regeneration or bioregeneration.

2.3.3.1 Bioregeneration

As can be seen from equation 2.6, free NH_4^+ can be liberated more quickly by increasing the solution concentration of another cation A^+, and forcing the equilibrium to the right. A strong solution of NaCl is typically used to chemically regenerate an ammonium saturated clinoptilolite column. However, the cost of chemical regeneration remains high and represents more than 50 - 60 % of the total process costs even with regenerant reuse (Koon and Kaufman, 1971). A potential solution to this problem is to use nitrifying bacteria oxidizing NH_4^+ to NO_3^-. The oxidation reaction should increase the rate of NH_4^+ desorption (eqn 2.6) by reducing the concentration of NH_4^+ in the bulk solution. One possible chemical equation, utilizing Na^+ as an exchange ion, and involving both ion-exchange and ammonium oxidation can be represented as:

$$S{:}NH_4^+ + NaCl + 2O_2 \rightarrow S{:}Na^+ + NO_3^- + H_2O + 2HCl \qquad \textbf{(2.8)}$$

There are a number of potential bioregeneration scenarios. They can be varied by both nitrifier placement with respect to the ammonium-saturated column, and the mode of providing supplemental oxygen or air. The nitrifying bacteria can be placed in the column (in-situ) with the ammonium-saturated clinoptilolite (Green *et al.,* 1996; Lahav and Green, 1998), or they could also be located in a separate reactor (ex-situ) from the ammonium-saturated column (Linne and Semmens, 1985; Semmens and Goodrich, Jr. 1977; Semmens *et al.,* 1977a; Semmens *et al.,* 1977b; Semmens, 1978; Semmens and Porter, 1979). In this instance the nitrifying biomass is either cycled through the clinoptilolite column with the regenerant or kept completely separate from the clinoptilolite. In the second case the regenerant is recycled through the clinoptilolite after the ammonium is removed by the bacteria. The ex-situ and in-situ bioregeneration scenarios are discussed next.

2.3.3.1.1 Ex-situ Regeneration

Semmens and others investigated both types of ex-situ processes. After an exhaustive study a separate nitrifying reactor was selected as the best method to recycle and reuse the regenerant. The purpose of the nitrifying biomass was to minimize the amount of regenerant necessary for regeneration, and not necessarily to enhance regeneration within the column. However, the results of his work are still important to this study. In the process regeneration is accomplished by treating the column with a concentrated salt solution (200 – 500 meq $NaNO_3$/L) and a culture of nitrifying bacteria which are separated from the effluent and regenerant by clarification. The process itself is patented (Semmens, 1978b).

Extensive batch studies with ammonium saturated clinoptilolite were conducted in the work leading up to the patent. Semmens and Goodrich, Jr. (1977) showed that the oxidation of ammonia is zero order with respect to ammonia concentration at high ammonium concentrations. however, the nonlinear relationship observed at low ammonium ion concentration indicates that the nitrification rate is a function of ammonium concentration most frequently below 30 mg/L. Semmens *et al.* (1977b) found in another study that the rate of nitrification was always independent (zero

order) of ammonium concentration above 1 mg N/L. In this case a nitrifying slurry was passed through a clinoptilolite column. The departure from zero order kinetics did not appear to be MLVSS, temperature or nutrient deficiency related. (Semmens and Goodrich, Jr., 1977). Chemically enhanced biological regeneration is quick process. Regeneration levels in the range of 70 - 80% were routinely achieved in a 1 - 3 hr time period depending upon MLVSS employed in the regeneration reactor (Semmens and Goodrich, Jr., 1977).

Nitrification rates were much slower during biological regeneration of the clinoptilolite than in reactors where ammonium was present in free solution without clinoptilolite (Semmens and Goodrich, Jr.,1977). The rate of nitrification during regeneration may therefore be governed by the rate at which ammonium becomes accessible (Semmens and Goodrich, Jr., 1977; Semmens *et al.*, 1977a). The rate at which ammonium desorbs from clinoptilolite would be the limiting factor nitrification rate and hence the regeneration rate. The tests used to reach these conclusions were all conducted at high initial solid-phase ammonium concentrations.

The rate of regeneration characteristically decreased as the extent of nitrification increased and was most pronounced in regeneration tests conducted with no added salt or with low salt (Semmens *et al.*, 1977a). Though Semmens *et al.*, (1977a) recommends using a saline solution to enhance nitrification, his data shows that greater than 95% regeneration can occur with no added salt; regeneration occurs at a much slower rate than when between 100 and 400 meq/L as NaCl is added. It should be noted that sodium should be the principal exchangeable ion in clinoptilolite ion-exchange applications (Eyde, 1995).

The studies conducted by Semmens and various other authors revealed some operational parameters that are important for design considerations. One important consideration is the reusability of the clinoptilolite. Semmens and Porter (1979) demonstrated the ability to achieve 90 to 97% regeneration over 43 loading cycles using a clinoptilolite column. Therefore, the exchange capacity is not reduced over the life of the clinoptilolite, and may not be a limiting factor in design.

Particle size also plays an important role in adsorption capacity, hydraulic conductivity, and exchange kinetics. There are trade-offs between hydraulic conductivity, adsorption capacity, and the adsorption and desorption kinetics. Czárán *et al.* (1988) found that ion-exchange capacity decreased with increasing particle size under dynamic conditions. Larger particles are preferred for their hydraulic conductivity, but Semmens *et al.* (1977a) found that approach to complete regeneration was always observed to be more rapid with particles of smaller size. As far as kinetics are concerned, this probably reflects the fact that more external surface exchange sites are available in a volume of smaller particles; ion-exchange can occur more rapidly at these unobstructed sites (Eyde, 1995).

Some concerns arise over the potential of the clinoptilolite column to foul when secondary wastewater is added to the column. The effluent from a CW is similar to secondary effluent wastewater. Linne and Semmens (1978), indicated that in one study performed by Battele-Northwest (1969), fouling occurred when unclarified secondary effluents were used; and in another study conducted by Murphy (1978) no loss of capacity and few operational problems occurred when the influent suspended solids level was between 20 and 50 mg/L. Linne and Semmens (1978) concluded in their study that operational problems were no greater in a clinoptilolite system which received unfiltered versus filtered wastewater. Semmens *et al.* (1977a) also found that no significant fouling occurred in clinoptilolite columns even when fed with solutions of humic acid materials. The only real biological growth occurred in the gravel sub-layer in the clinoptilolite column. In another study there was no fouling or permanent loss of exchange capacity when clinoptilolite was used over 43 loading and regeneration cycles with a synthetic secondary effluent (Semmens and Porter, 1979). McNair *et al.* (1987) studied the effect of clinoptilolite in slow-sand filtration on schmutzdecke characterization and found that the schmutzdecke adhered very little to the clinoptilolite. Equally important was the finding that there was no significant effect on the ion-exchange column efficiency caused by attached biomass (Green *et al.*, 1996; Lahav and Green, 1998). Thus, clinoptilolite does not easily foul.

2.3.3.1.2 In-situ Regeneration

Processes using an in-situ nitrifying biomass for regeneration are much more complicated than represented by equations (2.6) and (2.8). The biological regeneration process involves several steps, any of which can limit the rate at which the clinoptilolite is regenerated (See Figure 2.4).

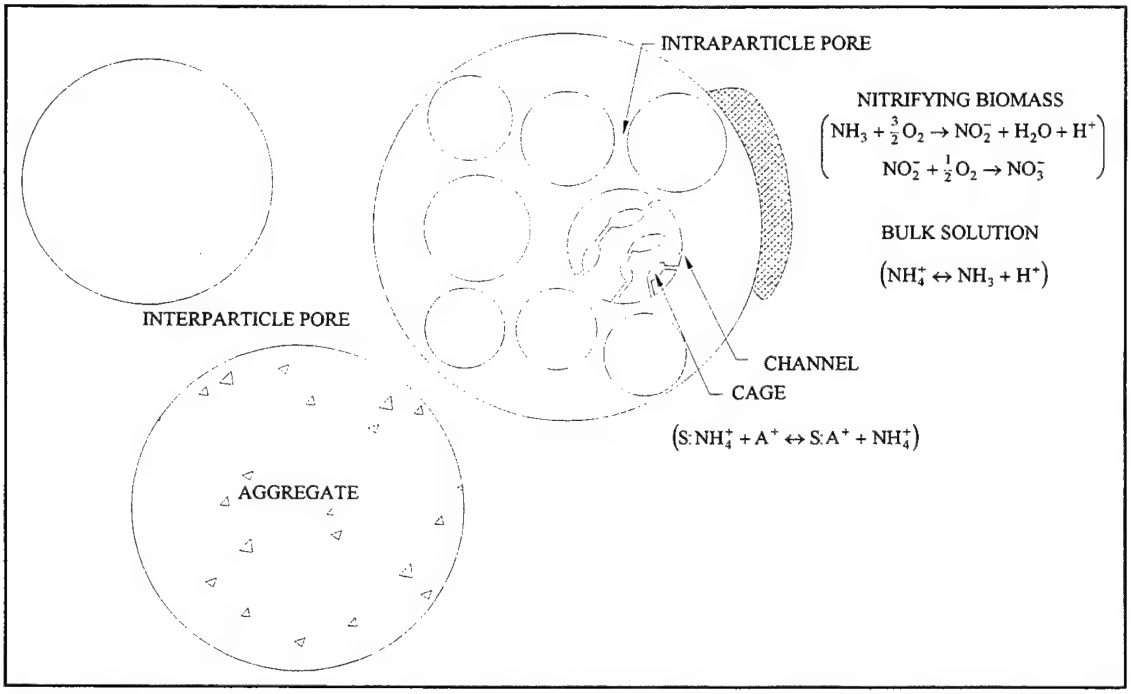

Figure 2.4: Chemical reactions occurring during bioregeneration. Reactions include ion-exchange, acid dissociation, and nitrification.

First, as shown in equation (2.6) ammonium must be desorbed to the bulk solution. This is a function of the availability of $S{:}NH_4^+$ exchange sites, the NH_4^+ bulk solution concentration and the concentration and type of exchange ions (A^+). Second, NH_4^+ must dissociate to NH_3 (eqn 2.9) so it can be used as substrate by nitrifiers (Shammas, 1986; Wood, 1986).

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad \textbf{(2.9)}$$

Third, *Nitrosomonas* convert the NH_3 to nitrite (NO_2-), and *Nitrobacter* oxidize nitrite to nitrate.

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^- \qquad \textbf{(2.11)}$$

$$NH_3 + \frac{3}{2}O_2 \rightarrow NO_2^- + H_2O + H^+ \quad \textbf{(2.10)}$$

There are several limiting factors that determine the rate at which equations 2.9, 2.10, and 2.11 will proceed. Equation 2.9 is a function of pH, temperature, and background NH_4^+ and NH_3 concentrations. Equations 2.10 and 2.11 are limited by substrate levels and O_2 availability, where the rate of oxidation is a function of how the bacterial population responds to temperature and pH. The entire bioregeneration process is dynamic since the available substrate concentration, or solid phase concentration decreases with time, which will drive the overall desorption process.

Several investigators used an in-situ nitrifying biomass. Green *et al.* (1996) and Lahav and Green (1998) used the zeolite as the carrier for the nitrifying biomass used to regenerate the clinoptilolite. In their study they used chabazite, instead of clinoptilolite, as the exchange media. During biological regeneration the column was used as a fluidized bed reactor operated batch-wise, utilizing pressurized oxygen along with sodium bicarbonate. The sodium bicarbonate was used to maintain pH and provide exchange ions for more efficient desorption. The in-situ, pressurized oxygen process configuration used by Green *et al.* (1996) reached a regeneration efficiency of 97% with a 10,000 mg/L Na^+ concentration, and a nitrification rate of 6 g $NH_4N/L_{reactor}$ /d using chabazite.

Lahav and Green (1998) concluded that the amount of NH_4^+ desorbed and its solution concentration are a function of the total cation concentration in the solution and the recirculation solution volume. They also stressed the importance of the solid phase NH_4^+ concentration on the rate of ammonium desorption, noting that the rate of desorption will decrease as the zeolite is regenerated, because the solid phase NH_4^+ concentration also decreases during regeneration. The maximal oxidation rate was achieved when NH_4N concentrations exceeded 5 mg/L. They concluded that tap water alone (10 meq/L) is not effective as a regenerant, because the cation concentration is too low to allow for a high enough NH_4^+ concentration with the respective nitrification rate. Lahav and Green (1998) concluded that the regenerant concentration should be at least 50 meq/L.

A major difference Lahav and Green found from Semmens' process was that the optimal regenerant concentration for their in-situ process should be much lower than the typical ion regenerant concentration used in ex-situ processes. Therefore, the process design must carefully balance the NH_4^+ desorption rate and nitrification rate to develop an efficient system. If the desorption rate is too high the NH_4^+ concentration can exceed discharge limits. The system may also be limited by oxygen or alkalinity. If the system is limited by the desorption rate (amount of regenerant) then the regeneration efficiency will be diminished.

In each of the studies previously listed, a sodium based regenerant (~ 0.3 M) and supplemental air/oxygen were used to enhance regeneration kinetics. These operational additions are more easily justified for a conventional treatment facility than a CW system.

CHAPTER 3
MATERIALS AND METHODS

This study was broken down into two parts. The first part of the investigation was a preliminary study that looked at the adsorption and desorption of ammonium on St. Cloud clinoptilolite in a batch reactor (isotherms), and the effect that conditioning the zeolite had on adsorption. The feasibility of using tap water and nitrifying bacteria to biologically regenerate clinoptilolite was also investigated during the preliminary study.

The second part of the study examined ammonium adsorption and desorption using a flow-through column. Bioregeneration studies were also conducted using two different regeneration schemes. The first scheme used an in-situ nitrifying biomass with in-situ diffused aeration. Tap water was continuously added to the column as a regeneration solution. The second process scheme also used an in-situ nitrifying biomass, but draw and fill cycles, using tap water, were used to regenerate the ammonium saturated clinoptilolite. In the second scheme, air for the bacteria was provided via passive aeration during the drain cycle. Two batch experiments were also conducted during this phase of the study; both investigated the effect the nitrifiers had enhancing the regeneration of the clinoptilolite.

3.1 Analytical Techniques

Based on the focus of the experiments, the parameters of interest were: NH_4^+, NO_3^-, NO_2^-, pH, DO, alkalinity, and temperature. The two most important factors that determine which method to use when deciding on an analytical method are the concentration of contaminants and the presence of interferences in the waste mixture. For

the purposes of this study, if more than one method met the criteria for the experiment then the simplicity of the method became the next most important factor.

3.1.1 Ammonia

The "Nesslerization Method" (4500-NH_3 C) was used for ammonia analysis (APHA, 1989). A double-beam, recording Shimadzu UV-VIS UV Spectrophotometer 160A (Shimadzu) was used analyze the samples. All samples were allowed to react with Nessler's Reagent for 30 minutes and analyzed using disposable cuvets at a wavelength of 415 nm.

3.1.2 Nitrate

The method selected for nitrate measurement was "Ultraviolet Spectrophotometric Screening Method" (4500-NO_3^- B) (APHA, 1989). The Shimadzu UV 160A spectrophotometer was used to analyze the samples with Fisher brand quartz cuvets.

When nitrite formation interfered with the above method then the "Ion Chromatograph Method" (4500-NO_2^- C) was used (APHA, 1989). A Dionex GP40 Pump was used with nitrogen gas to control eluent parameters. Undiluted eluent was pumped at a rate of 2 mL/min. The eluent used was 0.003 M $NaHCO_3$ and 0.0024 M Na_2CO_3. A Dionex CD20 Conductivity Detector was used in conjunction with a Dionex IonPac AG4A Guard Column and AS4A Column for analysis. The entire apparatus was controlled by a Dionex 4400 Integrator.

3.1.3 Nitrite

The method selected for nitrite measurement was "Ion Chromatograph Method" (4500-NO_2^- C) (APHA, 1989). The same apparatus, configuration and eluent used for nitrate analysis was also use for nitrite analysis.

3.1.4 pH

An Accumet dual frit pH probe coupled with an Accumet Model 50 pH, ion, conductivity meter is used for pH measurements. The apparatus was calibrated at least twice weekly.

3.1.5 Dissolved Oxygen

Dissolved oxygen (DO) is measured with a YSI Model 5239 probe and YSI Model 57 Oxygen Meter. The meter was calibrated in accordance with manufacturer's instructions. The apparatus was calibrated daily.

3.1.6 Alkalinity

Alkalinity was measured using the "Titration Method" (2320 B) (APHA, 1989). Hydrochloric acid was used for all titrations. Titrations were conducted with a 10 mL borosilicate glass buret. All samples were taken to a final pH endpoint of 4.50.

3.2 Preliminary Studies

3.2.1 Isotherm Adsorption Apparatus

The equipment used for the conditioning experiment included 125 mL erlenmeyer flasks, 100 mL and 1000 mL volumetric flasks, reagent grade sodium chloride NaCl, ammonium sulfate $(NH_4)_2SO_4$, ammonium chloride NH_4Cl, and a New Brunswick shaker table.

3.2.2 Isotherm Adsorption Methods

The purpose of this experiment was to look at the ammonium adsorption capacity of unconditioned and conditioned St. Cloud, 14-40 mesh, clinoptilolite. St Cloud, 14 -40 mesh, clinoptilolite was selected for several reasons. First, it is readily available; St. Cloud Mining is one of the largest producers of clinoptilolite in the United States (Eyde, 1995); and 14 - 40 mesh is a standard product. Second, a smaller size was

selected based on adsorption and desorption kinetics. The total exchange capacity is not affected by the particle size (Bernal and Lopez-Real, 1993), but kinetic exchange rates increase as particle size decreases (Semmens and Goodrich, Jr. 1977; Semmens *et al.*, 1977a). The experiment was conducted in three separate stages.

In the first stage, the adsorption capacity of unconditioned clinoptilolite was measured. In the second stage, the clinoptilolite was conditioned with alternating solutions of 1M NaCl, 0.25 M ammonium sulfate $(NH_4)_2SO_4$, and 1 M NaCl. In the third stage, the clinoptilolite was conditioned with 1 M NaCl.

3.2.2.1 Unconditioned Clinoptilolite

An ammonium chloride stock was prepared in accordance with APHA (1989). The strength of the stock solution was 1 mg NH_4N/mL. The stock solution was used to prepare working solution. Fifty milliliters of the stock solution were diluted to 1000 mL in a volumetric flask resulting in a 50 mg NH_4N/L working solution. Additionally, two 10 mL aliquots of the stock solution were diluted to 100 mL in volumetric flasks resulting in a 100 mg NH_4N/L working solution.

Ten different sized portions of St. Cloud, 14-40 mesh, clinoptilolite were weighed out and placed in 125 mL erlenmeyer flasks. Prior to weighing, the clinoptilolite was washed using deionized water and then dried at 103 °C. To eight of the clinoptilolite flasks, 100 mL of the 50 mg NH_4N/L working solution was added. The 100 mg NH_4N/L working solution was added to the other two flasks of clinoptilolite. The flasks were covered with parafilm, and placed on a New Brunswick shaker table at 300 rpm for 2 hours and 7 minutes. Ammonia analysis was conducted on the working solutions before they were added to the flasks containing clinoptilolite. Supernatant from each flask was filtered and analyzed for ammonia. Ammonium adsorption was calculated using the difference method.

3.2.2.2 NaCl-$(NH_4)_2SO_4$-NaCl Conditioning

The clinoptilolite and ammonium chloride stock solutions were prepared in the same manner as in section 3.2.1.2.1 (Unconditioned Clinoptilolite). Initially, 200 g of clinoptilolite were washed and dried for this part of the experiment.

Conditioning was first accomplished with a 1 M NaCl solution. The solution was prepared by adding 116 g of reagent grade NaCl to 2 L of deionized water. A Cole-Palmer Stir-Pak was used to mix the solution in a 4 L beaker. The clinoptilolite was added to the NaCl solution and stirred vigorously for 2 hours. The contents of the beaker were drained and then rinsed three times with deionized water.

Subsequently, 61 g of $(NH_4)_2SO_4$ were added to 2 L of deionized water resulting in approximately a 0.25 M $(NH_4)_2SO_4$ solution. The solution was added to the rinsed clinoptilolite and mixed using the Stir-Pak for 2 hours. Again the clinoptilolite was drained and rinsed three times with deionized water.

As a final conditioning treatment, the rinsed clinoptilolite was mixed for 2 hours with a 1 M NaCl solution using the Stir-Pak. The clinoptilolite was drained and rinsed three times with deionized water and put in an oven at 103 °C to dry.

As in the previous experiment, 10 different samples of conditioned clinoptilolite were weighed out and placed in 125 mL erlenmeyer flasks. Three different ammonium chloride working solutions were prepared for this part of the experiment. A 50 mg NH_4N/L working solution was prepared in the same manner as in the previous section. A 100 mg NH_4N/L solution was prepared by diluting 20 mL of the stock solution to 200 mL in a volumetric flask, and a 200 mg NH_4N/L working solution was prepared by diluting 20 mL of stock solution to 100 mL in a volumetric flask. Each flask was analyzed for ammonia content prior to adding to the conditioned clinoptilolite. One hundred milliliters of working solution (50 mg NH_4N/L) were added to seven of the erlenmeyer flask. The 100 mg NH_4N/L working solution was split between two flasks, and the 200 mg NH_4N/L working solution was added to one of the erlenmeyer flasks. The flasks were placed on a New Brunswick shaker table at 300 rpm for 2 hours.

The supernatant was filtered and analyzed for ammonia. Ammonium adsorption was calculated using the difference method.

3.2.2.3 NaCl Conditioning

This part of the experiment was conducted in the same manner as in section 3.2.1.2.3 (NaCl-$(NH_4)_2SO_4$-NaCl Conditioning), except that the clinoptilolite was conditioned for 2 hours with a 1 M NaCl solution. Three working solutions of 200, 100, and 50 mg NH_4N/L were also prepared as in the previous section, however, only one aliquot of 100 mg NH_4N/L was used in this part.

3.2.3 Batch Conditioning-Optimization Apparatus

The purpose of this experiment was to look at the effect of varying NaCl solution concentrations on ammonium adsorption in clinoptilolite. The equipment used for the conditioning experiment included 125 mL erlenmeyer flasks, 1 L volumetric flasks, reagent grade NaCl and NH_4Cl, and a New Brunswick shaker table.

3.2.4 Batch Conditioning-Optimization Methods

The clinoptilolite was washed with deionized water to remove any fines and dried at 103 °C for two days and then placed in a desiccator until it was used. Six different NaCl solutions were prepared with deionized water by diluting 9.9364 g, 19.2846 g, 29.2311 g, 33. 1577 g, 49.0800 g, and 58.4442 g of reagent grade NaCl in one-liter volumetric flasks.

Seven 25.0 g aliquots of St. Cloud, 14-40 mesh, clinoptilolite were placed in 125 mL erlenmeyer flasks with 100 mL of each of the different NaCl solutions and one with 100 mL of deionized water. The flasks were put on a New Brunswick shaker table at 300 rpm for two hours and thirty minutes to condition the clinoptilolite. The flasks were drained and rinsed six times each to remove any residual NaCl, and put in a 103 °C oven overnight to dry, and placed in a desiccator to cool.

An ammonium chloride solution was prepared by diluting 75 mL the NH_4Cl stock solution (1 mg NH_4N/mL) to 1000 mL in a volumetric flask resulting in a 75 mg NH_4N/L solution. The ammonium concentration was measure in the feed solution using nesslerization. One hundred milliliters of the ammonium solution were added to each flask of clinoptilolite; the flask was placed on a New Brunswick shaker table at 300 rpm for two hours. All samples were filtered using a 0.45 μm nitrocellulose filter, and analyzed using nesslerization. The difference method was used to calculate the ammonium adsorbed.

3.2.5 Biological Regeneration Feasibility Study Apparatus

Three different types of reactors were used in the initial biological regeneration feasibility studies. They included a simple beaker with a mechanical stirrer, a prefabricated glass column with a fine glass-frit diffusor, and a glass-jacketed Cytolift™ Bioreactor used in conjunction with a constant temperature bath. The last two reactors proved to be failures and are not discussed in this thesis.

3.2.5.1 Batch Biological Regeneration Reactor

Four one liter beakers and a Phipps and Byrd gang-stirrer (See Figure 3.1) were used for the clinoptilolite biological regeneration feasibility study.

3.2.5.2 Nitrifying Bacteria Reactor

The nitrifiers used for this study were obtained from nitrifying reactor used in another unrelated study (Chen, 1998). The culture was grown in a 20 L, amber-colored plexiglass tank. The tank was divided by a baffle that separated a 15 L aeration zone from a 5 L settling zone. A rectangular diffusor stone was used for both aeration and mixing. The mixed liquor suspended solids (MLSS) concentration was maintained at 3000 mg/L. Approximately 350 mL was wasted from the aeration zone each day. Nitrifying bacteria for this study were obtained from this waste solution.

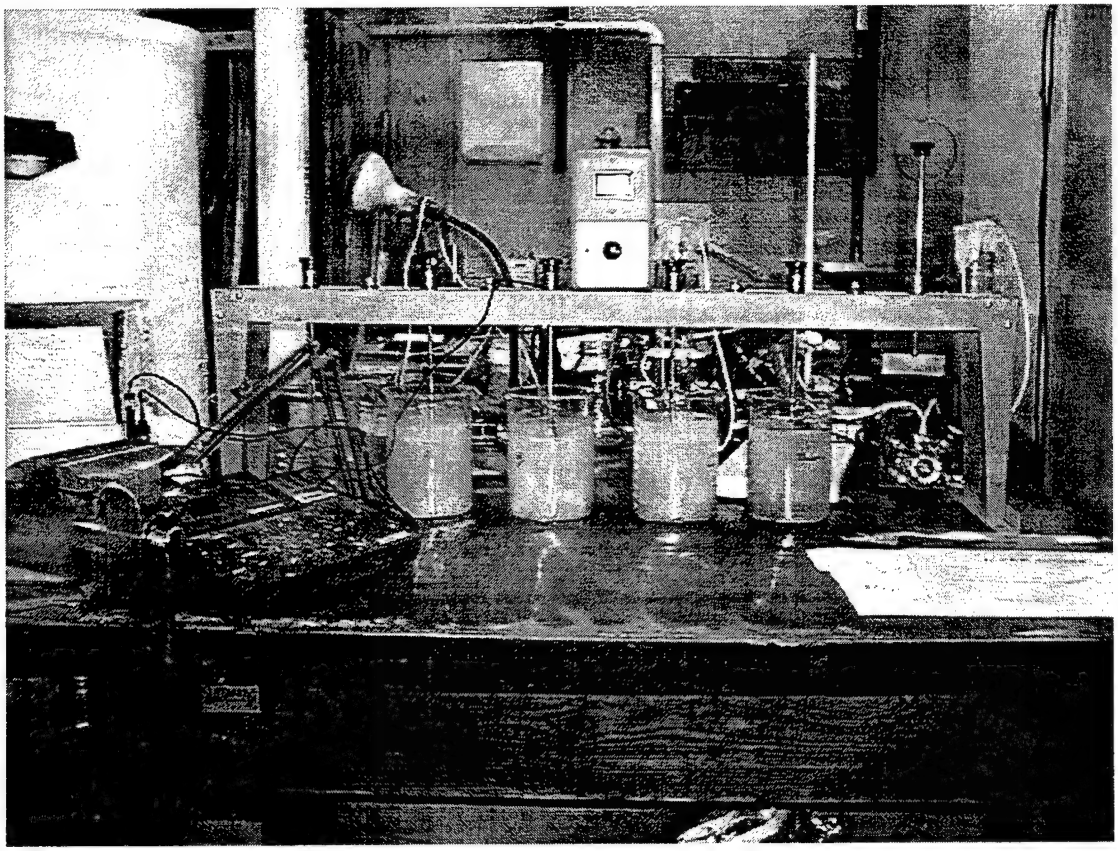

Figure 3.1: Batch reactors used for biological regeneration feasibility study.

The culture was fed a mixture of 5.64 g/L ammonium bicarbonate (NH_4HCO_3), 3 g/L sodium bicarbonate ($NaHCO_3$), 0.034 g/L potassium phosphate monobasic (KH_2PO_4), 0.087 g/L potassium phosphate dibasic (K_2HPO_4), and 0.0708 g/L sodium phosphate dibasic (Na_2HPO_4) in tap water. Sodium bicarbonate ($NaHCO_3$) was used to maintain a pH of 7.5 to 7.6. A pH controller coupled with a diaphragm pump was used to supply the necessary base.

3.2.6 Biological Regeneration Feasibility Study Methods

3.2.6.1 Batch Reactor

St. Cloud, 14 - 40 mesh, clinoptilolite was used for this series of experiments. A complete description of the physical properties of St. Cloud clinoptilolite can be found in Appendix A. The clinoptilolite was triple rinsed using deionized water to

remove any excess fines and allowed to dry at 103 °C overnight. Approximately 130 g of dried clinoptilolite were added to a ten liters of 50 mg NH_4N/L ammonium chloride solution for 2 hours. The solution was analyzed for ammonium prior to adding the clinoptilolite. The supernatant was analyzed for ammonium after the 2 hour adsorption period. Ammonium adsorption was calculated using the difference method.

The clinoptilolite was drained and triple rinsed with deionized water to remove any excess ammonium chloride solution. The clinoptilolite was allowed to air dry overnight. Five equal portions of clinoptilolite were weighed out (35 g each). The clinoptilolite was not completely dry when the samples were weighed. Three of the portions were used for the regeneration experiment and the other two were dried at 103 °C and placed in a desiccator to give an average dry weight for the samples. The average dry mass of the two samples was 21.4 g.

The other three portions were placed in one liter beakers that were labeled A, B and C. Each beaker was filled with 1 L of tap water that had been aerated overnight to dechlorinate it. The tap water was also filtered (0.45 μm) to remove iron hydroxides produced by aeration. The typical cation concentration of the tap water was: $Li^+ = 0.3$, $Na^+ = 11$, $K^+ = 3$, $Mg^{2+} = 38$, and $Ca^{2+} = 98$ mg/L. Twenty-five milliliters of washed nitrifiers were added to each beaker.

A control was also used; 95.5 mg of NH_4Cl was added to 1000 mL of the same tap water used in the other reactors resulting in a 25 mg NH_4N/L solution. The same amount of nitrifiers were added to the control beaker. The reactors were mixed at 150 rpm with the Phipps and Bird gang stirrer. After the first series of experiments, the entire apparatus was covered with a large cardboard box to reduce the inhibition effects of light on nitrifiers.

Ammonium, NO_3^-, pH and DO were measured at various time intervals in each reactor, but the time between sampling periods was never more than three days. Dissolved oxygen measurements were abandoned after levels remained above 6 mg/L. Any evaporated water was replaced with nanopure water before sampling for mass balance purposes. The reactors were shut down when the nitrate level had stabilized.

This same experiment was repeated three times reusing the same clinoptilolite in each reactor. Controls were used for only the first two experiments in this series. Before reusing the clinoptilolite in each beaker, the contents of the beaker were drained and rinsed four times with deionized water. Washed nitrifiers (25 mL) were added to each beaker after the clinoptilolite was saturated with ammonium and quadruple rinsed with deionized water.

3.2.6.2 Nitrifying Bacteria Preparation

The nitrifiers were washed to remove any excess inorganic salts, particularly NH_4^+ and NO_3^-, that might be present in the nitrifier reactor solution. The waste suspension was centrifuged (Bausch-Lomb Model 50) for 10 minutes at 6000 rpm and then decanted. After decanting the sludge was resuspended with nanopure water, it was centrifuged again as described above. Washing was repeated followed by one final centrifugation. The bacteria were then ready to be used for the biological regeneration experiments. Note that this method was used to prepare the nitrifiers for all experiments. Total suspended solids were measured several times after this washing procedure and averaged about 1300 mg/L. It is assumed this represents almost entirely nitrifying bacteria.

3.3 Column Studies

Two different reactor configurations were used in the column biological regeneration studies. Both used an in-situ nitrifying biomass, but differed in their aeration and regenerant application methodology. The first reactor used an in-situ diffused aeration mechanism, and regenerant was continuously added to the clinoptilolite column. The second generation reactor used draw and fill batch methodology; the drain cycle provided air for the bacterial biomass via passive aeration.

3.3.1 In-Situ Diffused Aeration Biological Regeneration Apparatus

3.3.1.1 1st and 2nd Prototype Columns

Three different types of columns were built for the first generation biological regeneration experiment. Both are similar, but some changes were necessary because of some operational problems discovered with the 1st and 2nd prototypes. Three 3rd prototype columns were finally constructed.

Batch-mode was used to saturate the clinoptilolite with ammonium in the 1st and 2nd prototype columns. A separate, continuous flow adsorption experiment was performed on the three 3rd prototype reactors. The 1st prototype column was constructed using a 4 in. ID acrylic tube (See Figure 3.2). Three inches of ¾ in. and three inches of ¼ in. river washed rock were added to bottom of the column. This configuration failed when air was supplied to the column (Figure 3.3). The mixing caused by the aeration allowed the clinoptilolite to short circuit through the drainage system.

The 1st prototype was modified by replacing the base layer with six inches of washed filter sand, a rubber gasket (Figure 3.4 and Figure 3.5), and geotextile geotextile (Contech Construction Products AP HBC, unwoven, 7 oz/yd^2) filter. The gasket dislodged when air was used to scour the column.

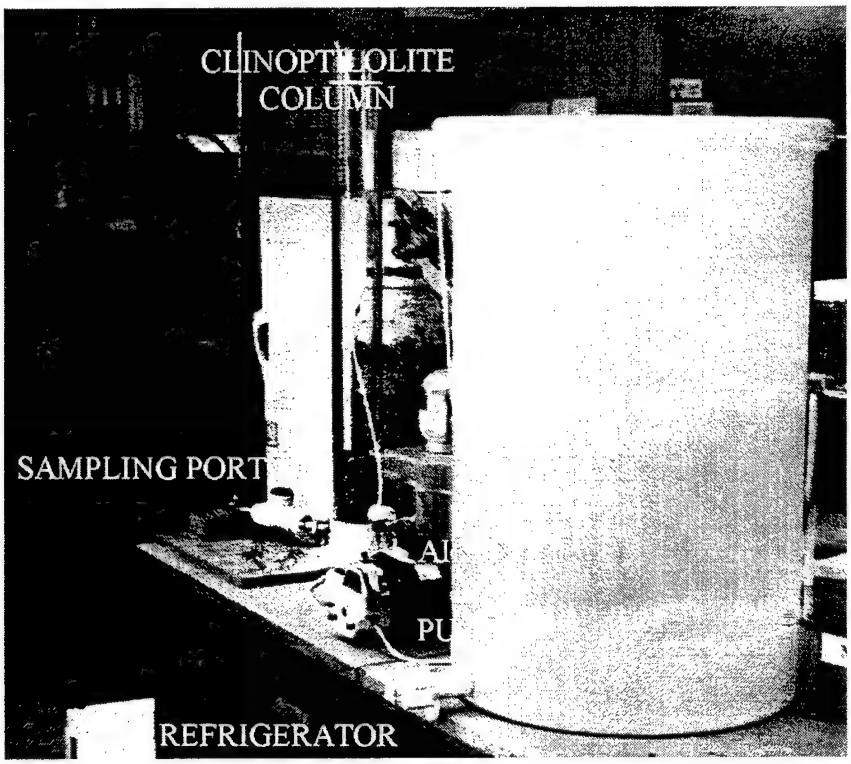

Figure 3.2: First prototype continuous flow biological regeneration reactor. Support media is in the column. The clinoptilolite has not been added to the plexiglass column.

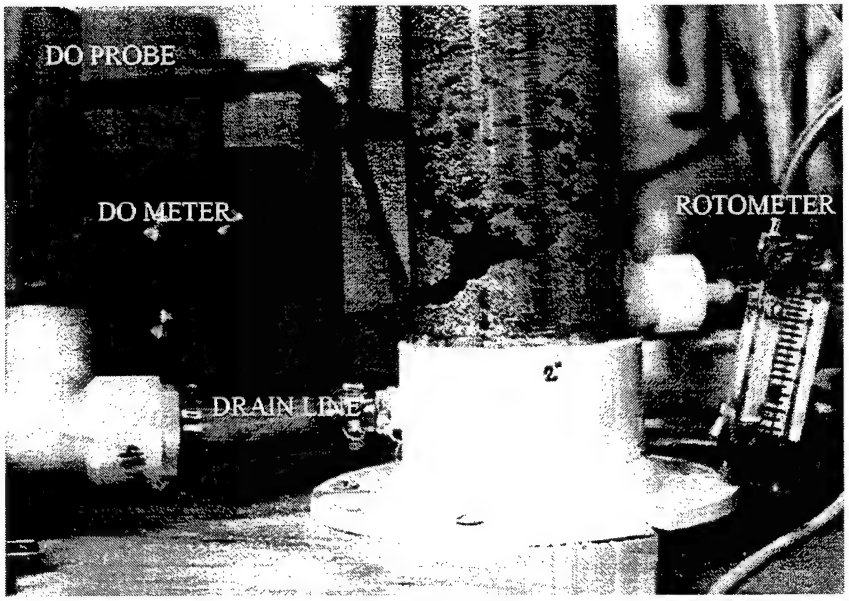

Figure 3.3: First prototype continuous flow reactor. Clinoptilolite had short circuited through the column drainage system.

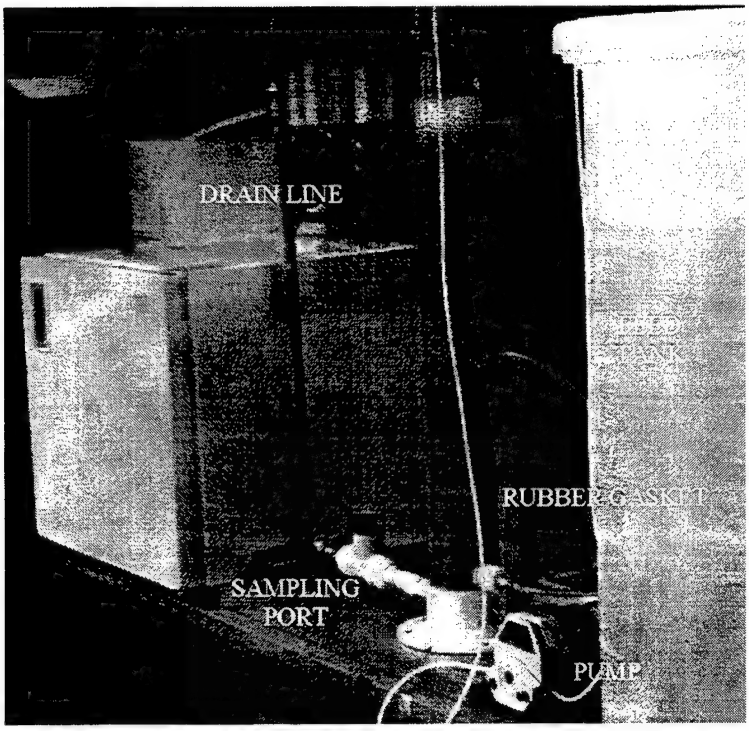

Figure 3.5: Second prototype continuous flow biological regeneration reactor being regenerated.

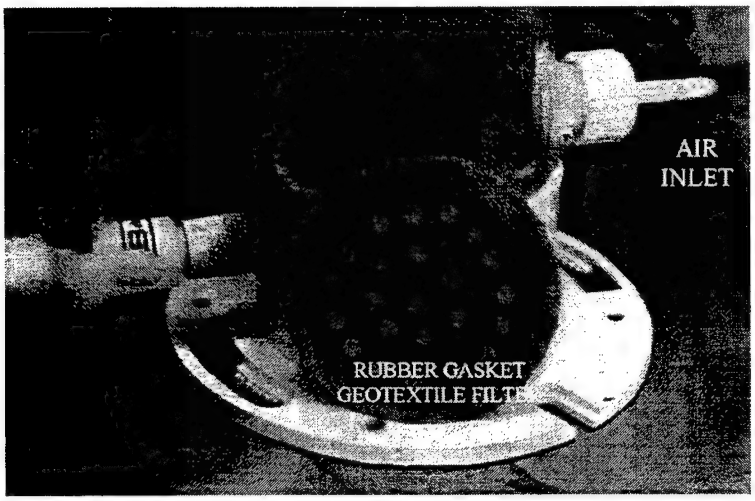

Figure 3.4: Second prototype continuous flow biological regeneration reactor. Six inches of sand were used as support media. The gasket-filter was placed between the sand and the clinoptilolite. The effluent line was changed from poly tubing to CPVC.

3.3.1.2 3rd Prototype Column Apparatus

The 3rd prototype (Figure 3.6) was constructed using 4 in. ID PVC tubing

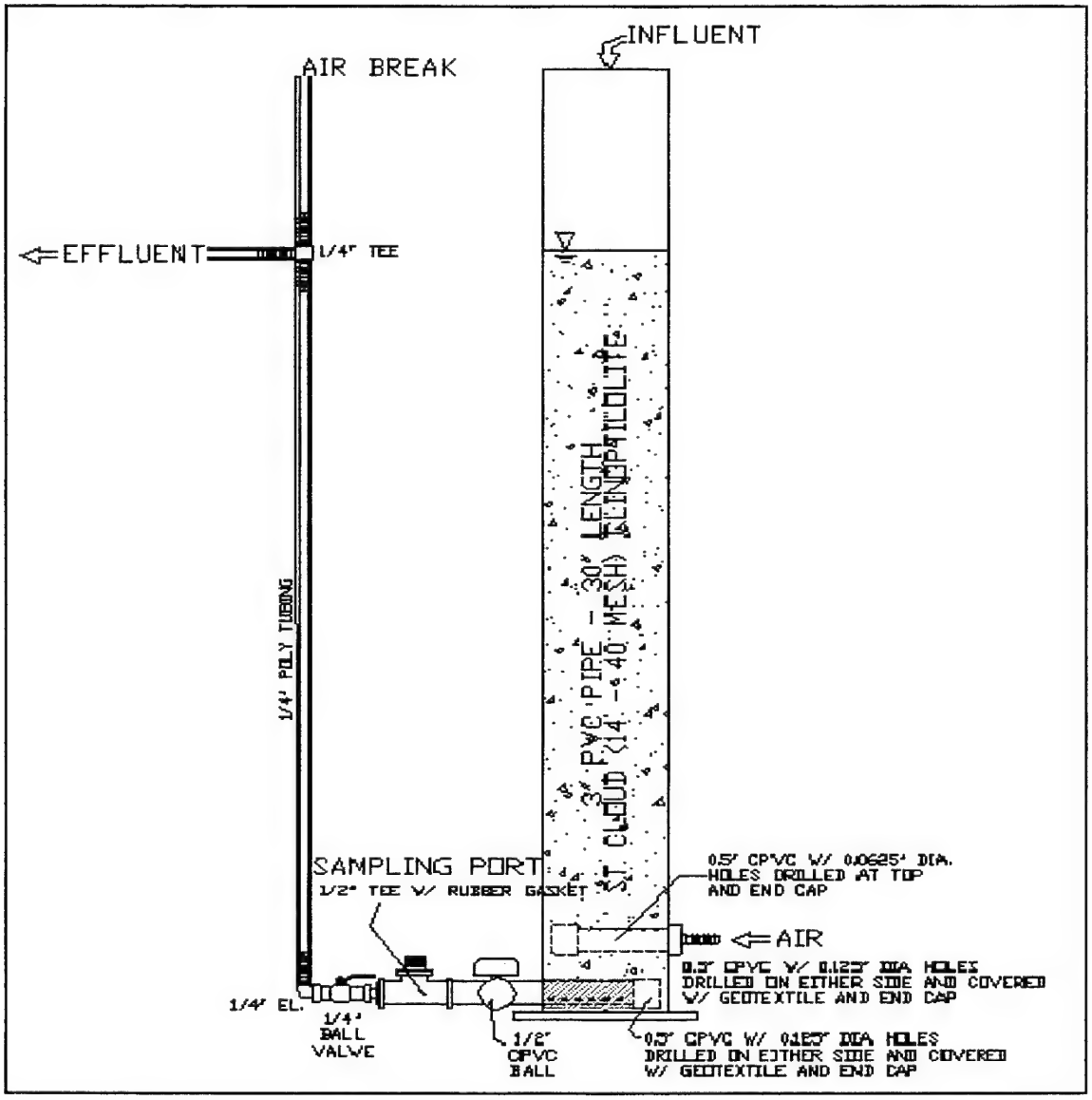

Figure 3.6: Schematic of the 3rd prototype continuous flow biological regeneration reactor.

instead of plexiglass. The drainage system was also modified. The CPVC drainage tube was wrapped with the geotextile (Contech Construction Products AP HBC, unwoven, 7 oz/yd^2) and epoxied to prevent the clinoptilolite from exiting the column. The sand and

filter mechanism kept the bulk clinoptilolite particles from exiting the column, but not any fines produced during the bioregeneration process.

3.3.1.3 3rd Prototype Column Methods

3.3.1.3.1 Adsorption Phase

Continuous-flow (Figure 3.7) was used to saturate the clinoptilolite in the 3rd prototype in-situ diffused aeration reactors. Seven thousand grams of St. Cloud, 14-40

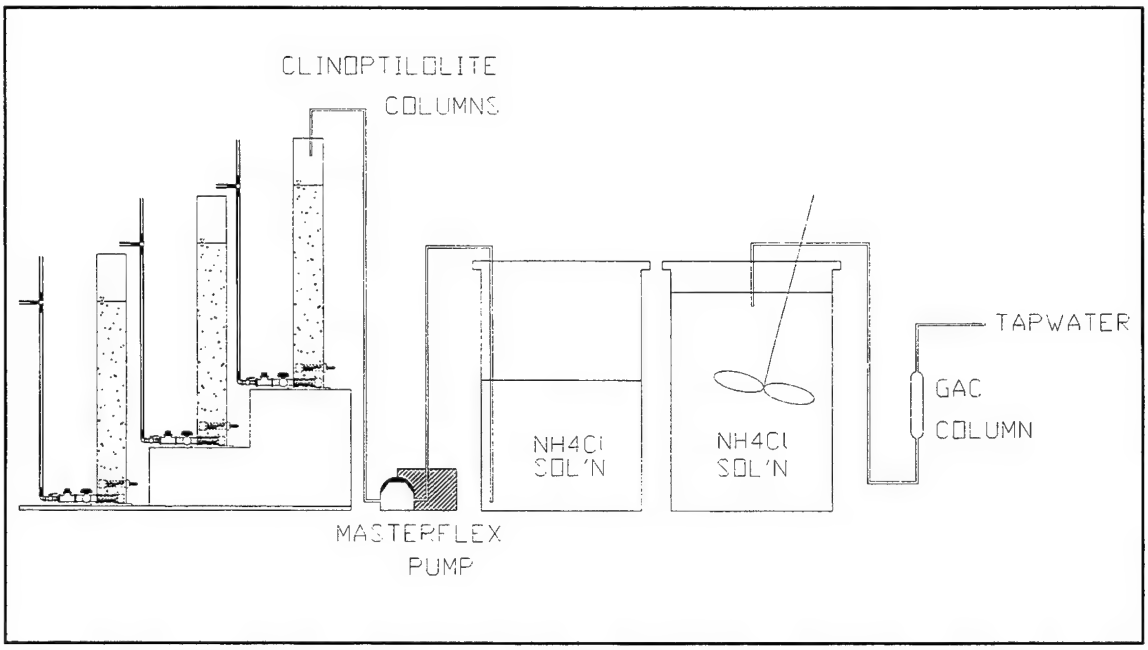

Figure 3.7: Adsorption schematic for continuous flow reactor. Feed water flowed from the highest reactor the lowest using differential head.

mesh, clinoptilolite was conditioned, for three days, in 5 gallons of a 0.5 M NaCl solution prepared with tap water. The NaCl solution was drained and the clinoptilolite was rinsed three times with tap water to simulate realistic process conditions. The conditioned and rinsed clinoptilolite was mixed with 400 mL of washed nitrifiers. The clinoptilolite-nitrifier slurry was divided among the three columns (Column #1, #2, and #3). The depth of clinoptilolite in each column was 21.5 in., 23 in., and 22.25 in. respectively. Aerated tap water was added to each column before it was placed in a 4°C constant temperature

room. The columns were temperature equilibrated for one day before the adsorption experiment was started.

An ammonium chloride feed was prepared using tap water treated with the GAC filter to remove residual chlorine. Initially, 10.9 g of NH_4Cl was added to two 30 gallon nalgene containers which should yield an approximate ammonium concentration of 25 mg NH_4N/L. Subsequently, NH_4Cl was added based upon the amount of tap water needed to refill the tank and maintain the feed concentration at approximately 25 mg NH_4N/L. Ammonium was measured in the feed tanks after each new batch of feed was prepared.

The three columns, hooked in series, were fed through the first column with a Masterflex peristaltic pump. Ammonium was measured in the effluent from each column at varying time intervals. A three-inch extension was added to Column #1 because of back-fill problems. The experiment was stopped before breakthrough occurred in the third column, because of clogging problems. Two days into the adsorption experiment samples were analyzed for nitrate, but none was found.

3.3.1.3.2 Regeneration Phase

Before starting the regeneration phase the columns remained in the 4°C room for three additional days. After three days the columns were moved to a 15°C constant temperature room. Two of the columns (#2 and #3) had leaks so they were drained and warmed up before the leaks were repaired with silicon.

Tap water, that had been aerated to remove excess chlorine, was added to the two repaired columns after the silicon had been allowed to dry for 24 hours to recheck for leaking. Column #2 still had a leak and regeneration was not immediately attempted. The column remained in the 15°C room for several more days.

For the regeneration cycle the drain lines were adjusted to ½ in. above the clinoptilolite in the corresponding column. The Masterflex pumps were calibrated with a graduated cylinder and stop watch. Initially, the pumping rate was set at 6.4 and 7.5

mL/min for column #1 and column #3 respectively. Rotometers were used to control the air flowrate into each column. The flowrate was set at 1 L/min for each column.

The regenerant pumping rates were measured during the course of the experiment. Minor deterioration of the tubing caused some variations in the pumping rate. The pumping rate was monitored daily after the deterioration problem was discovered.

Ammonium, nitrate, pH, and DO were measured throughout the experiment. A composite sample was used for column #1. The effluent was collected in a refrigerator (4°C). A hole was drilled into the top of the refrigerator so that the column effluent tube would drain into a beaker on the inside of the refrigerator. A grab sample was used to measure DO in all columns. Grab samples were used for Column #3 for ammonium and nitrate analysis. Dissolved oxygen measurements were abandoned when the DO was well above 2 mg/L. Alkalinity was measured in the feed and periodically in the columns.

Three days into the regeneration experiment 250 mL of nitrifiers were added to the top of column #1. It was later discovered that the nitrifier reactor was not working properly and that the nitrifiers that were added to the column may not be viable. A couple of days were allowed for the nitrifier reactor to recover before more nitrifying bacteria were added to column #1. Another 250 mL of nitrifiers were added, to Column #1, 12 days after the regeneration experiment was started. The 250 mL of washed nitrifiers was resuspended with 100 mL of nanopure water; 60 mL and 40 mL were injected at 12 in. and 18 in. from the bottom of the column respectively.

When clogging occurred in the columns, air was used to scour the columns. The flowrate was increased to 10 L/min for 5 min. Initially, this alleviated clogging problems. However, column #1 was removed from service 42 days after the regeneration experiment was started. The column was sacrificed to see why the feed solution would not flow through the column.

Column #2 was moved from the 15°C room, nine days after it was initially put in there, to a lab (~ 22°C). The leak was patched again with silicon and

allowed to dry for 24 hours. The column was filled with tap water with no leaks noted. Approximately 2 L of tap water was poured through the column of which 1.95L was collected. The leachate was analyzed for ammonium and nitrate. The Masterflex pump was adjusted to a flow rate of 10.1 mL/min. An aerated, tap water feed was maintained in a covered stainless steel container to reduce algal growth in the feed and column.

Six days after starting regeneration on column #2 nitrifying bacteria were added. Again, 250 mL were washed and resuspended with 100 mL of nanopure water. Aliquots of 50 mL, 30 mL, and 20 mL were added to the column at 12 in., 18 in., and to the top of the column respectively.

Seven days after the regeneration began on Column #2, the feed was backing-up over the top of the column. Air scouring did not alleviate the problem. The column was drained and all the clinoptilolite was removed, rinsed, and put back in the column. All leachate was collected and analyzed for nitrate and ammonium. The regeneration experiment was stopped 27 days after it started because the feed started backing-up over the top of the column again.

3.3.2 Draw and Fill Passive Aeration Biological Regeneration

3.3.2.1 Adsorption Apparatus

The adsorption phase was done using continuous flow. Two different columns were constructed for the adsorption experiment. One was constructed with two feet of 1.25 in. ID acrylic tube (column A) and the other with three feet of 1" ID PVC (column B). Column A was tapped (1 in. MPT) so that the filter apparatus and top cap could be screwed directly into the column. A 1" FPT coupling was glued to the top and bottom of column B so that the filter apparatus and top cap could be connected to the column. The columns and adsorption process diagrams are shown in Figures 3.8 and 3.9 respectively.

The filter apparatus used to retain the clinoptilolite in both columns incorporated two PVC couplings, rubber gaskets, geotextile fabric, and sand. The

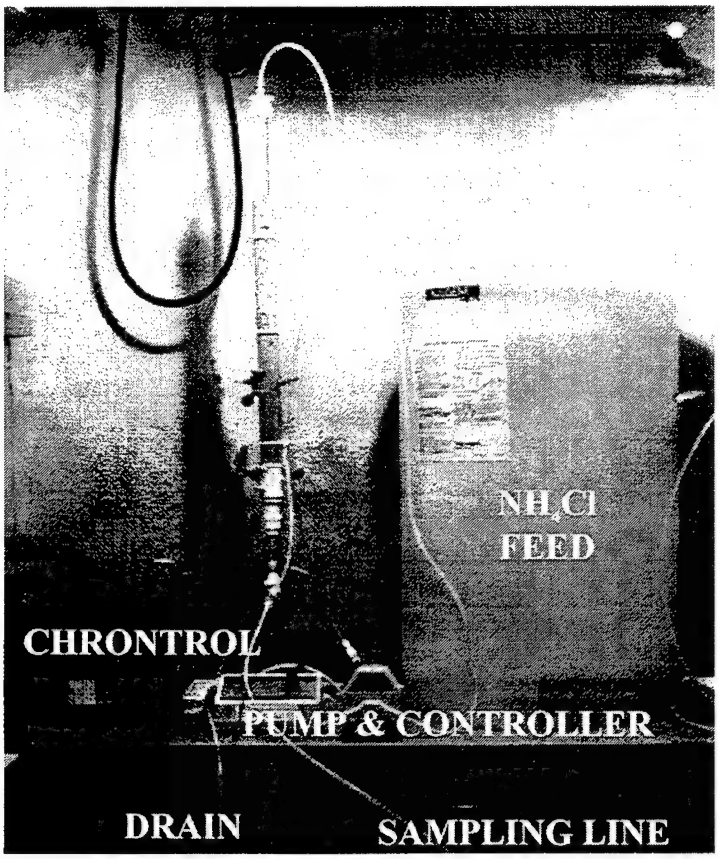

Figure 3.8: Adsorption experiment using acrylic column.

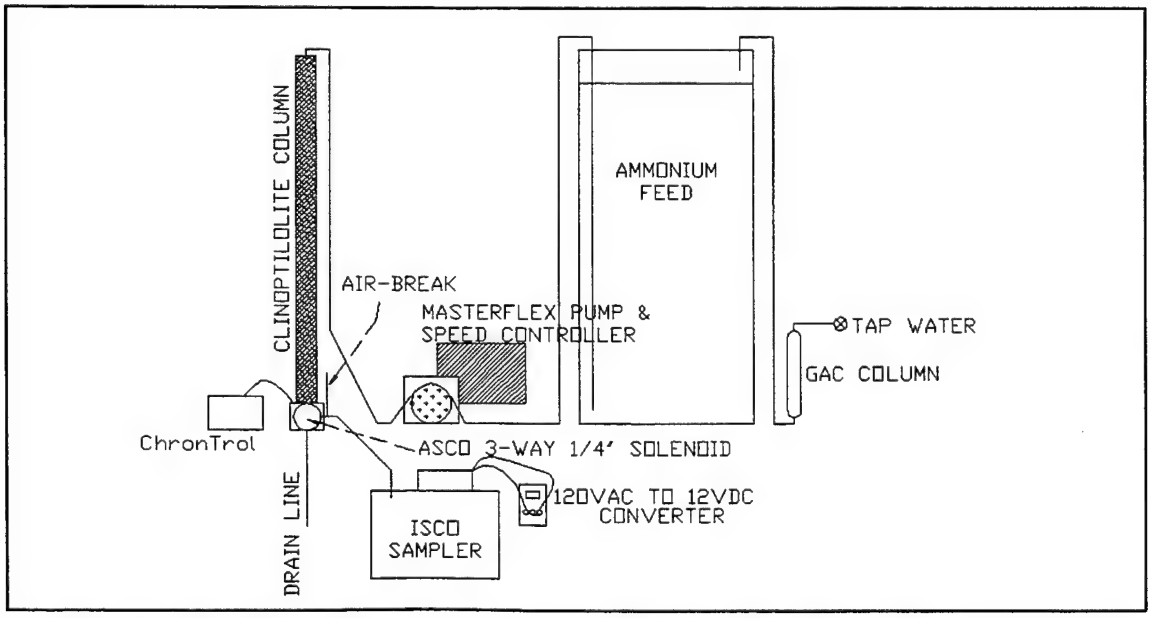

Figure 3.9: Adsorption schematic for draw and fill bioregeneration column.

geotextile (Contech Construction Products AP HBC, unwoven, 7 $oz \cdot yd^{-2}$) was sized for the openings on the couplings and sandwiched and epoxied between two rubber gaskets. The gaskets were glued into place at each of the openings. Washed filter sand was put into the smaller coupling, and the larger coupling was slid over the top of the smaller one and glued in place.

3.3.2.2 Adsorption Methods

St. Cloud clinoptilolite, 14-40 mesh, was conditioned in a 0.5 M NaCl solution for three days, rinsed with tap water and allowed to dry at 103 °C overnight and placed in a desiccator with NaCl. Two hundred-fifty mL of washed nitrifiers and 250.0 g of the dried clinoptilolite were added to the column in lifts. Column A and column B had dry volumes of 324 mL and 334 mL respectively ($\gamma_{bulk, avg}$ = 760 $kg \cdot m^{-3}$). Deionized water was added to the column to completely saturate it. The top cap was screwed on and sealed with silicon to prevent leaking. It was allowed to dry overnight at room temperature, to cure the silicon, and was then placed in the 4 °C room for an additional day before the adsorption experiment was started. Adsorption was done at 4 °C to simulate worst case conditions for an effluent from a constructed wetland.

A Masterflex pump was calibrated to 5 empty bed volumes per hour (BV/hr) or 27.2 mL/min. A ¼", 3-way ASCO valve was connected to the bottom of the column. The valve was plugged into circuit #1 on the Chrontrol timer and was programmed to open for 5 minutes every hour. This allowed 5 minutes of sample to be collected in the ISCO sampler every hour. The effluent from the column ran into a floor drain during the remainder of the run.

The ISCO sampler was modified for the adsorption experiment. Part of the pumping mechanism was removed from the ISCO sampler so that the sampler would still function, but could use gravity flow, instead of a pump, to fill the sample containers. The ISCO was programmed to rotate to the next sampling station every hour. The ISCO program was executed five minutes before the Chrontrol program.

Ammonium for the feed tank was prepared by adding 10.9 g of NH_4Cl to approximately 30 gallons of tap water that was purified with the OMNIFILTER™ GAC filter. The GAC filter was used was to remove chlorine from the tap water. Ammonium-spiked tap water was used as a feed to simulate a wetland effluent where nitrification was not functioning. The ammonia concentration in the feed averaged 26 mg NH_3N/L. A typical medium strength wastewater has a free ammonia concentration of 25 mg NH_3N/L (Tchobanoglous and Burton, 1991). The water was allowed to equilibrate to 4 °C before the experiment was started. Ammonia concentration was measured using nesslerization in both the feed tank and effluent sample bottles. The adsorption experiment lasted 24 hours and 30 minutes.

The second adsorption experiment (column B) was conducted in the same manner except for the following differences. The Masterflex pump was calibrated at 2.1 BV/hr (11.4 mL/min), the 3-way solenoid valve was programmed to open for 12 minutes every hour for sampling, and the experiment was run until ammonium concentration in the effluent was above 1 mg/L, but less than 2 mg/L. The ammonia concentration in the feed averaged 26 mg NH_3N/L.

3.3.2.3 Regeneration Apparatus

The same setup was used for the regeneration phase, except that the feed tank was filled with aerated tap water, and the effluent from the column was drained into a refrigerated beaker. The cap was removed from the top of the column to allow air to flow into the column during the drain cycle. See Figure 3.10 for a schematic of the regeneration process. The three way solenoid used for the adsorption phase was replaced with two larger 2-way solenoid valves to enhance drainage. An ASCO 3/8" FPT, 2-way, normally closed valve was connected to column A. A MAGNATROL Valve Corp., ½" FPT, 2-way, normally-open valve was connected to column B. A normally open valve was selected for the second experiment in hind sight after the first regeneration experiment had been started. The column would not overflow if the valve failed or there was any type of electrical failure.

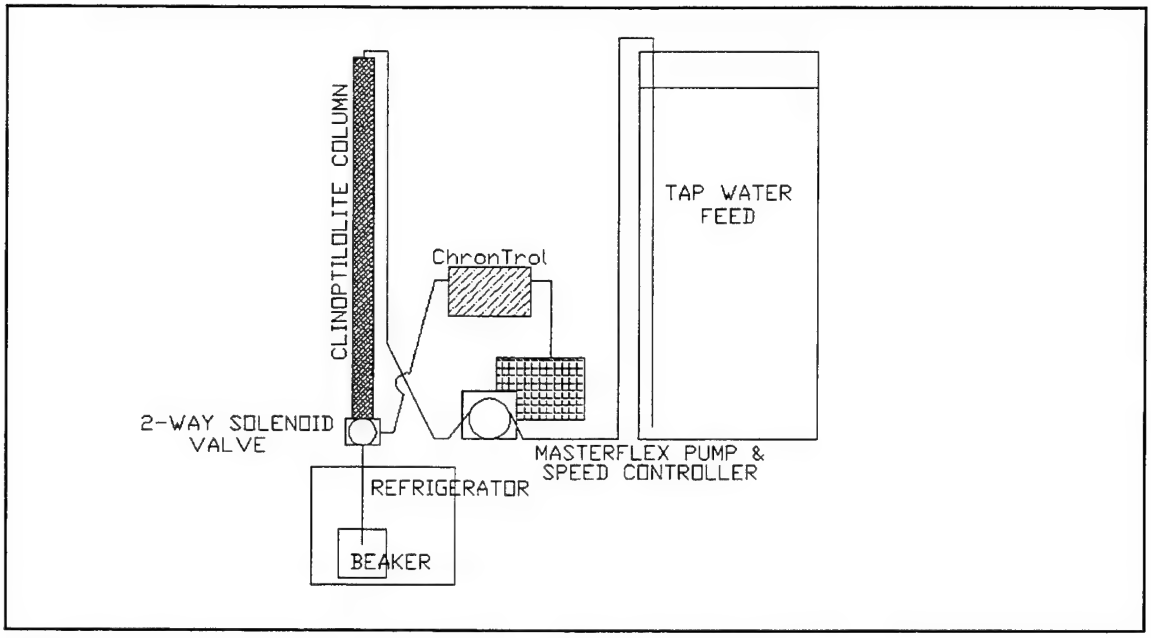

Figure 3.10: Regeneration schematic for draw and fill column.

3.3.2.4 Regeneration Methods

3.3.2.4.1 Column A Parameters

After the adsorption experiment was completed column A was left in the 4°C room for an additional 5 days and then placed in a 15°C constant temperature room, drained, and left overnight to temperature equilibrate. The temperature in the constant temperature room was set at 15°C, but fluctuated between 13°C and 15°C with an average temperature of 14°C. Column A was placed in the constant temperature room (14°C) to simulate the worst anticipated conditions that might be used for biological regeneration. Column B remained in the 4°C for 4 days after the adsorption experiment, and was subsequently drained and moved to a lab (20°C ±). It was left overnight to temperature equilibrate.

One bioregeneration cycle per day (cyc/d) was selected as a starting point for the feasibility investigation of column A. Initially, a programmable timer was not used for the column A bioregeneration study. The column was filled with 120 mL of the

feed water (tap water) once per day for two hours and then allowed to drain the remainder of the 24 hour period. Tap water was used as a regenerant because the ion concentration was considered representative of a wetland effluent, and micro nutrients needed for the nitrifiers were available in the tap water. The process worked well, but it would take 164 days to completely regenerate the column assuming the rate of regeneration remained constant and did not decrease with time.

After 10.8 days a solenoid valve was added to column A along with a Masterflex peristaltic pump, and both were connected to a Chrontrol programmable timer. The timer was initially programmed so that the pump would turn on for 30 seconds twice per day at 12 hour intervals (2 cyc/d). Approximately 120 mL of feed water were pumped during the 30 second period. The feed water was allowed to remain in the column for two hours and then the solenoid was opened and the effluent from the column was drained into a refrigerated sampling beaker. All of the effluent was collected and analyzed for mass balance purposes. The process continued to work well, but based on the data for 2 cyc/d it was determined that it would take 73 days to regenerate the column.

After an additional 20 days the timer was reprogrammed for three cyc/d based on the success of the previous increase, and to see if the rate of regeneration could be increased even further. Based on an analysis of the data, regeneration would take 71.5 days. There was little benefit gained by increasing the number of regeneration cycles to three per day, but based on the stage of regeneration the number of cycles was not changed back to 2 cyc/d.

3.3.2.4.2 Column A Feed Contamination

The tap water used to regenerate column A was not spiked with ammonium. However, it was determined that there was approximately 3.1 mg N/L (NH_4^+, NH_3, NO_3^-, NO_2^-) of contamination in the feed. The source of contamination was unknown. After the contamination was discovered, the feed was changed and monitored

with each effluent sample. The effluent mass-balance data were adjusted for the feed contamination.

3.3.2.4.3 Column B Parameters

The timer for column B was adjusted to 2 cyc/d The pump was turned on for 5 minutes, but still pumped approximately 120 mL of feed (tap water spiked with ~ 2 mg/L NH_4Cl). The feed pumping rate was decreased so that the column would not airlock during the fill cycle. The timer was programmed so that the valve would remain closed for a two-hour time period during and after the column was filled. The valve was open for the ten hour drain cycle.

The feed for column B was spiked with NH_4Cl (2.1 mg/L), which may always be present in the wetland effluent, to see what effect a small input of ammonia would have on the bioregeneration process.

3.3.2.4.4 Nitrite Formation in the Feed

After 28 days nitrite was present in the feed and the ammonia concentration had decreased slightly. The nitrite continued to increase and reached a maximum at 36 days, when the ammonia feed concentration was near zero. The feed was changed, and spiked again with NH_4Cl (2.2 mg NH_4N/L). Nitrite was present again in the feed 12 days after the switch. All of the ammonia eventually converted to nitrite. The feed for column A had the same problem. The feed for column B was monitored, but not changed for the duration of the experiment, because the influent ammonia had very little effect on the effluent ammonia concentration.

The feed problem (nitrite formation) in both columns was traced to a contaminated diffusor stone used to aerate the tap water. The tap water was aerated for 24 hours to remove any chlorine from the tap water. An inspection revealed a green film covering the stone. From an intuitive perspective one would assume that the ammonium/ammonia would all be converted to nitrate since the feed was well oxygenated. More than likely, bacteria that oxidize ammonia to nitrite (i.e. *Nitrosomonas*)

were present in the feed, but nitrite oxidizing bacteria (i.e. *Nitrobacter*) were not present. This hypothesis was not investigated, since the nitrite formation had no impact on the bioregeneration experiment.

3.3.2.4.5 Sampling

The composite effluent for both experiments were analyzed for ammonium, nitrate, nitrite, pH, and alkalinity. Feed composition was analyzed at the same sampling interval as the column B effluent. Nitrite and alkalinity were not analyzed in column A immediately at the start of the experiment. The volume of each composite sample was measured using a 250 mL graduated cylinder.

3.3.3 Draw and Fill Batch Biological Regeneration Studies

Two laboratory-scale experiments were used to look at the influence of the nitrifying biomass on the regeneration of ammonium-sorbed clinoptilolite. The purpose of the first experiment was to examine the effect of nitrifier concentration on the rate of regeneration. The second laboratory-scale batch experiment was conducted to see what effect the presence of nitrifiers had on the regeneration rate using tap water and deionized water.

3.3.3.1 Experiment #1 Apparatus and Methods

Three 125 mL erlenmeyer flasks were used in the first experiment and filled with 50 mg of the same clinoptilolite prepared for the column experiments, and stored in the desiccator. Ammonium was adsorbed by adding 100 mL of 1500 mg NH_4N/L of NH_4Cl to the flasks and shaking on a shaker table (New Brunswick) at 300 rpm for 2 hours. The solid phase concentration was 2.63, 2.63, and 2.54 mg NH_4N/g clinoptilolite for flask A, B, and C respectively. Measurements were based on the difference method.

No nitrifiers were added to the control (flask A), while 30 mL (washed), and 90 mL (washed) were added to flasks B and C respectively. The clinoptilolite was

bioregenerated at 14°C. Forty mL (1 cyc/d) of tap water was used as a regenerant for seven days in the first experiment. The regenerant was added for two hours and then decanted through a 0.45 μm filter.

3.3.3.2 Experiment #2 Apparatus and Methods

Four 250 mL erlenmeyer flasks were used in the second experiment, also using the same clinoptilolite. Ammonium was adsorbed by adding 100 mL of 1200 mg NH_4N/L of NH_4Cl, prepared with nanopure water, to the flasks and shaking on a shaker table (New Brunswick) at 300 rpm for 2 hours. The solid phase concentration was 2.19, 2.18, 2.22, and 2.23 mg NH_4N/g clinoptilolite for flask A, B, C, and D respectively. Measurements were based on the difference method. Each flask of clinoptilolite was subsequently triple rinsed with deionized water.

Nanopure water was used as a regenerant for flasks A and C while GAC-filtered tap water was used for flasks B and D. Twenty-five mL of washed nitrifiers were added to flasks C and D. The clinoptilolite was bioregenerated at 22°C ±. Forty mL (1 cyc/d) of tap water was used as a regenerant for six days in the second experiment. The regenerant was added for two hours and then decanted through a 0.45 μm filter.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Adsorption Experiments - Preliminary Studies

4.1.1 Conditioning

The purpose of the adsorption experiments was to examine the effect that different types of chemical conditioning (pretreatment) have on the adsorption capacity of the clinoptilolite. Three different conditioning scenarios were investigated: NaCl, alternating treatments of NaCl-$(NH_4)_2SO_4$-NaCl, and no conditioning. Koon and Kaufman (1971) summarized several studies where NaCl was used as the primary conditioning agent. Semmens and Porter (1979) and Lahav and Green (1998) used a similar alternating treatment process in pilot scale studies. Although no reason was cited for the intensified conditioning process, Dr. Semmens (personal correspondence, 1997) revealed that the total adsorption capacity achieved was superior using this technique, but he also concluded that it would not be cost effective for process application.

In its unconditioned state, clinoptilolite is typically saturated with Na^+, K^+, Mg^{2+} and Ca^{2+} ions (Czárán *et al.*, 1988). The amount and type of saturation varies with the source of the clinoptilolite. In its raw state, St. Cloud clinoptilolite is 2 % potassium and 2.7 % calcium by weight. The purpose of the conditioning step is to convert the exchange sites to a preferred ion form. Sodium is the preferred ion form when clinoptilolite is used for ion-exchange applications (Eyde, 1995). Since clinoptilolite has a higher affinity for NH_4^+ than Na^+ the ion-exchange during adsorption is more efficient.

4.1.1.1 Purpose

In a process application the clinoptilolite is conditioned once before it is put into service. Reconditioning is unnecessary because the clinoptilolite is essentially reconditioned during regeneration. Haralambous *et al.* (1992) determined in their research that for ammonium removal the conditioning step could be avoided, since the loading and unloading of the zeolite could act as a conditioning step too. These findings were not confirmed when unconditioned clinoptilolite was used in this study. One difference may be that adsorption studies were done at low NH_3N concentrations.

4.1.1.2 Langmuir Isotherm and Modeling

The results of the conditioning experiments are summarized in Figure 4.1. The data from all three experiments were modeled using a Langmuir isotherm. The data were evaluated for both Freundlich and Langmuir isotherms using a Marquardt-Levenberg nonlinear regression. The Langmuir model yielded the best results. Bernal and Lopez-Real (1993) also found that ammonium adsorption in clinoptilolite was best represented by a Langmuir isotherm. The Langmuir isotherm is given by:

$$\frac{C_s}{C_{s,max}} = \frac{K_L C_w}{1 + K_L C_w} \qquad \textbf{(4.1)}$$

Where C_s is the mg NH_4N/g clinoptilolite, $C_{s,max}$ is the maximum amount of NH_4N adsorbed when every available exchange site is occupied, K_L is the Langmuir coefficient which is an empirical constant (L/mg NH_3N), and C_w is the NH_3N bulk solution concentration (mg NH_3N/L). The limitations of the Langmuir model are: (1) the assumption that the energy of adsorption is independent of the degree of coverage, (2) reversibility of bonding, and (3) allowance for at most only one monolayer (Montgomery, 1985).

The assumptions used to develop the Langmuir model fit the ammonium-clinoptilolite ion-exchange process well. In the ion-exchange process the monolayer can be related to the available exchange sites, because there are a finite number of exchange sites available for adsorption. Since ion-exchange involves the adsorption and desorption

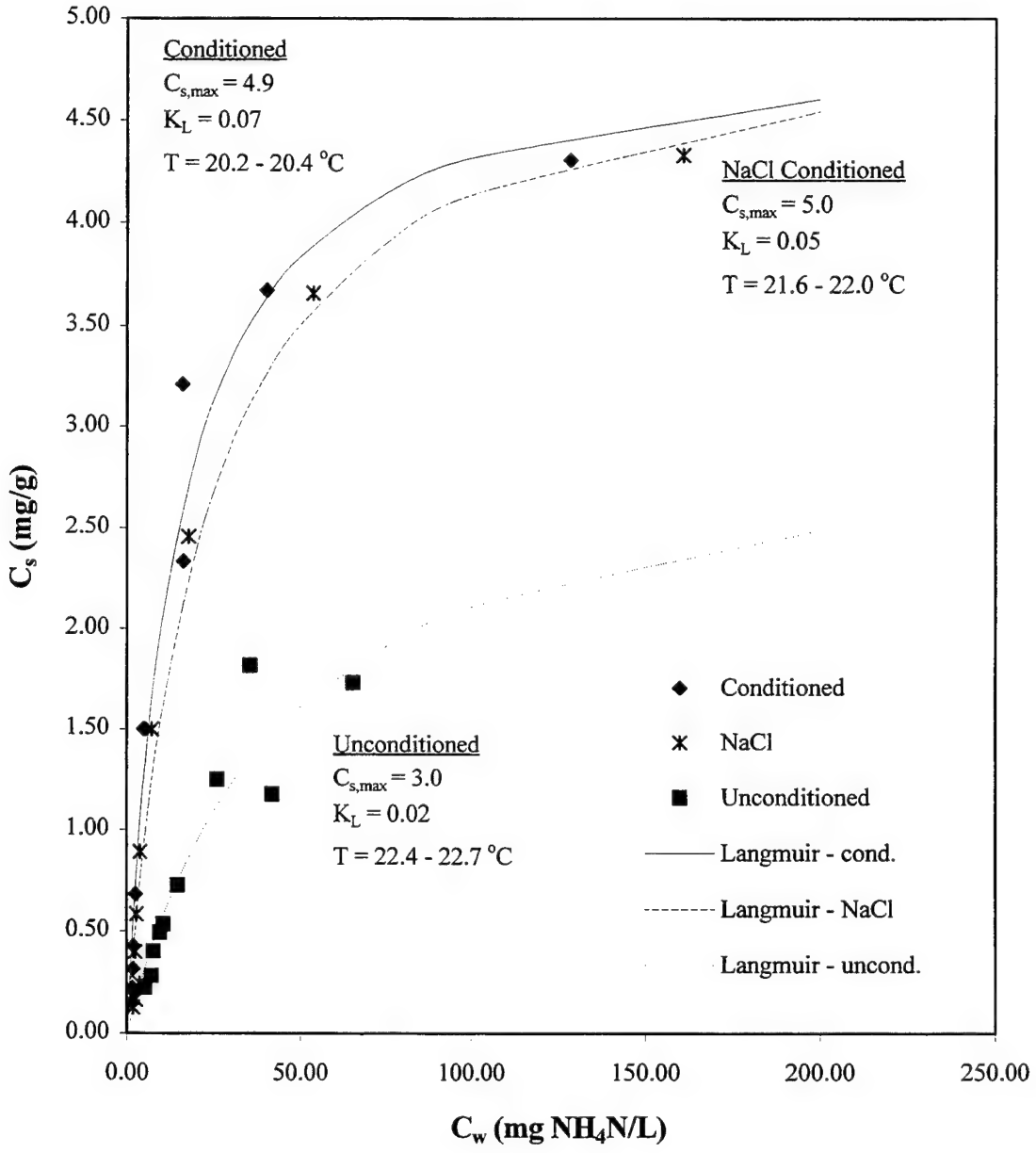

Figure 4.1: Raw isotherm data and corresponding Langmuir curve for each data set. St. Cloud, 14 - 40 mesh, clinoptilolite was used for all three experiments.

of a target ion the process inherently requires reversibility of bonding. However, the assumption that the energy of adsorption is independent of the degree of coverage is not totally valid. Divalent ions require two adjacent sites for adsorption, and therefore as the number of occupied exchange sites increases the energy required for a divalent ion to occupy two adjacent sites also increases. In addition, the channel and cage size varies within the zeolite crystal, therefore more energy is required to reach the exchange sites located within the smaller channels and cages.

4.1.1.3 Effectiveness of Conditioning

Chemical conditioning has a big effect on the adsorptive capacity of St. Cloud clinoptilolite. The total adsorption capacity is increased over 1.7 times by using chemical conditioning. The total adsorption capacity, $C_{s,max}$, was 4.93, 5.04, and 3.05 mg NH_4N/g clinoptilolite for NaCl-$(NH_4)_2SO_4$-NaCl, NaCl, and no conditioning respectively. Not only is there a substantial increase in adsorptive capacity, but the effect conditioning has on the Langmuir coefficient is even more important, because of its application to the entire study.

Every subsequent experiment done for this study was based on a medium strength municipal waste with an influent ammonium concentration of 25 mg NH_3N/L. Based on this, the columns used in the CW process will be operating in the linear portion of the Langmuir isotherm where K_L is more influential.

The Langmuir coefficient, K_L, was 0.07, 0.05, and 0.02 L/mg NH_3N for NaCl-$(NH_4)_2SO_4$-NaCl, NaCl, and no conditioning respectively. Chemical conditioning results in a three-fold increase in adsorptive capacity at low NH_3N concentrations. Assuming an influent concentration of 25 mg NH_3N/L, the total adsorptive capacity is 3.1, 2.7, and 1.1 mg NH_4N/ g clinoptilolite for NaCl-$(NH_4)_2SO_4$-NaCl, NaCl, and no conditioning respectively. Chemical conditioning increases the adsorption capacity by 145 % and 185 % for NaCl and NaCl-$(NH_4)_2SO_4$-NaCl conditioning respectively. However, the benefit derived by intensified conditioning is minimal. NaCl-$(NH_4)_2SO_4$-NaCl results in a 17% increase in adsorptive capacity over NaCl conditioning.

4.1.1.4 Process Application and Decision Making

The final decisions on the type and degree of conditioning are based on some important considerations. First, cost. Cost must include the cost of chemicals, plus any process modifications that are required for conditioning the clinoptilolite, and any cost of disposing of the spent reagent. This cost must be compared to the cost of additional clinoptilolite, real-estate, reactor size, and what effect if any the additional clinoptilolite will have on the process design.

The second consideration is process simplicity. One of the main benefits of CWs is the low technology required to operate them. Therefore, it is important that the chemical conditioning process be as simple as possible, especially since conditioning is required only once. To this end, NaCl conditioning was selected. The reactor size is an important consideration in the clinoptilolite process. The reactor size for unconditioned clinoptilolite is twice the size of one that uses conditioned clinoptilolite. The NaCl-$(NH_4)_2SO_4$-NaCl conditioning process is too prohibitive for the 17% increase in adsorptive capacity (influent 25 mg NH4N/L). The cost of the chemicals would be at least tripled and it will be much more difficult to get rid of that amount of spent conditioner, especially since it contains a very high concentration of ammonium (0.25 M). The next step was to optimize the conditioner concentration.

4.1.2 Optimizing NaCl Conditioning

The purpose of this experiment was to optimize the concentration of NaCl required to effectively condition the clinoptilolite prior to ion-exchange activities. Most researchers that used NaCl as a conditioner reported no basis as to why they selected a 1 M concentration. The optimum NaCl concentration needed to condition the clinoptilolite is an important consideration in the process design. Any decrease in the chemical requirements results in an overall decrease in capital costs. The results of the experiment (See Figure 4.2) show that there is little benefit gained by increasing the NaCl concentration above 0.5 M during conditioning. Therefore, chemical costs for

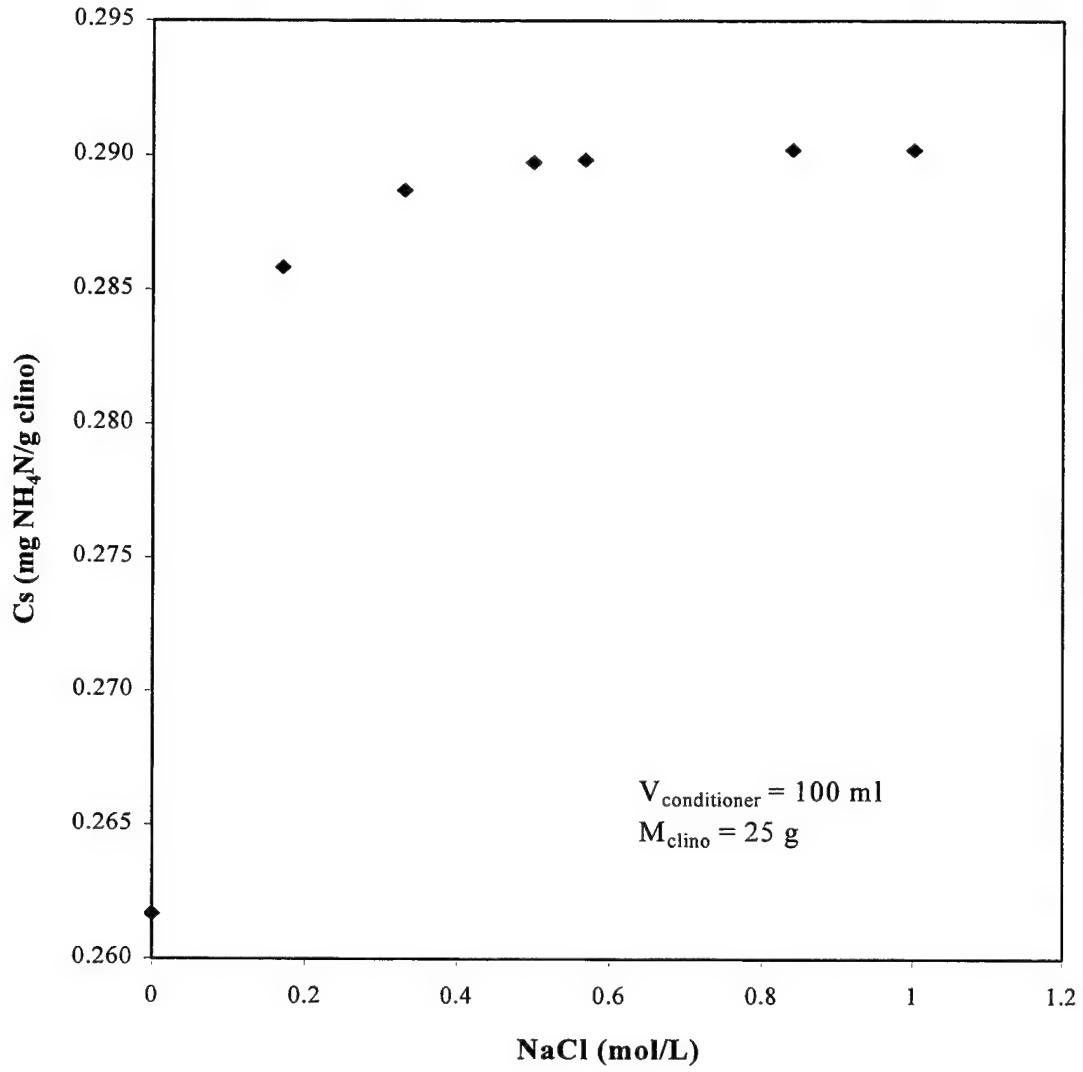

Figure 4.2: Optimizing NaCl concentration for clinoptilolite conditioning.

chemical conditioning can be reduced by one-half by decreasing the concentration of NaCl solution used for conditioning by one-half.

4.2 Bioregeneration Feasibility - Phase 1

4.2.1 Batch Study

These experiments were designed to investigate the feasibility of using in-situ nitrifiers and tap water to regenerate ammonium-saturated clinoptilolite. The experiments are similar to those of Semmens and Goodrich, Jr. (1977); but unlike their experiments, these experiments were accomplished at low mixed liquor suspended solids (MLSS) concentrations and low solid-phase ammonium concentrations.

4.2.1.1 Adsorption

All of the clinoptilolite used for the first experiment was loaded with ammonium in one batch, and then divided between the three beakers. The solid-phase concentration was 0.81 mg NH_4N/g clinoptilolite. After each regeneration experiment the clinoptilolite was washed using deionized water. This was done to remove any residual nitrate produced during the regeneration experiment. For the subsequent experiments, the clinoptilolite in each beaker was loaded with ammonium individually.

There was no apparent degradation in the adsorptive capacity over the entire series of experiments. The solid-phase concentration was 1.02, 0.96, and 1.03 mg NH_4N/g clinoptilolite for beakers A, B, and C respectively, in the second series. The solid-phase concentration, for the third series, was 0.88, 0.94, and 0.90 mg NH_4N/g clinoptilolite for beakers A, B, and C respectively.

4.2.1.2 Bioregeneration

The bioregeneration experiments were conducted using 4 one-liter beakers. Three contained ammonium-saturated clinoptilolite, nitrifiers, and tap water was used as a regenerant. The fourth beaker was used as a control with no clinoptilolite.

4.2.1.2.1 Control

A control was used for the first two bioregeneration cycles. The purpose of the control was to compare the nitrification rate in the control to that of the beakers that contained clinoptilolite. A mass of NH_4N equal to the amount of NH_4N adsorbed to the clinoptilolite was added to the control reactor along with an equal amount of washed nitrifiers. All of the other conditions were the same.

Ideally, the control should have a higher nitrification rate because the ammonium is more readily available for oxidation. Semmens and Goodrich, Jr. (1977) determined that the rate of nitrification was higher when ammonia was degraded without the presence of clinoptilolite. However, in this study, the rate of nitrification was equal to or slightly lower in the control than in the beaker containing clinoptilolite during the first regeneration experiment (See Figure 4.3). Light inhibition was thought to be a possible reason for this discrepancy. The beakers containing the clinoptilolite were cloudy, and light may not have effected them in the same manner as the control.

The beakers were shielded from light for the second series of regeneration experiments, and this time the control had an equal or slightly higher nitrification rate than the other clinoptilolite-containing reactors (See Figure 4.4), but there is not a significant difference between the control and the clinoptilolite-containing reactors. These results do not necessarily validate the findings of Semmens and Goodrich. Jr. (1977). However, the experiments done for this study were conducted at a much lower initial NH_3N concentrations; about $1/8^{th}$ of those in the Semmens' study. The size of the clinoptilolite in the Semmens study was also slightly larger (18 - 50 mesh), which would result in a slower desorption rate (Semmens, 1978).

Ammonium desorption can be characterized by exponential decay (Figure 4.5). These findings are similar to those of Semmens *et al.* (1977b). Initially, ammonium desorption from the clinoptilolite is faster than the rate of nitrification. Figure 4.6 is representative of the three beakers (A, B, and C) used in the 2^{nd} and 3^{rd}

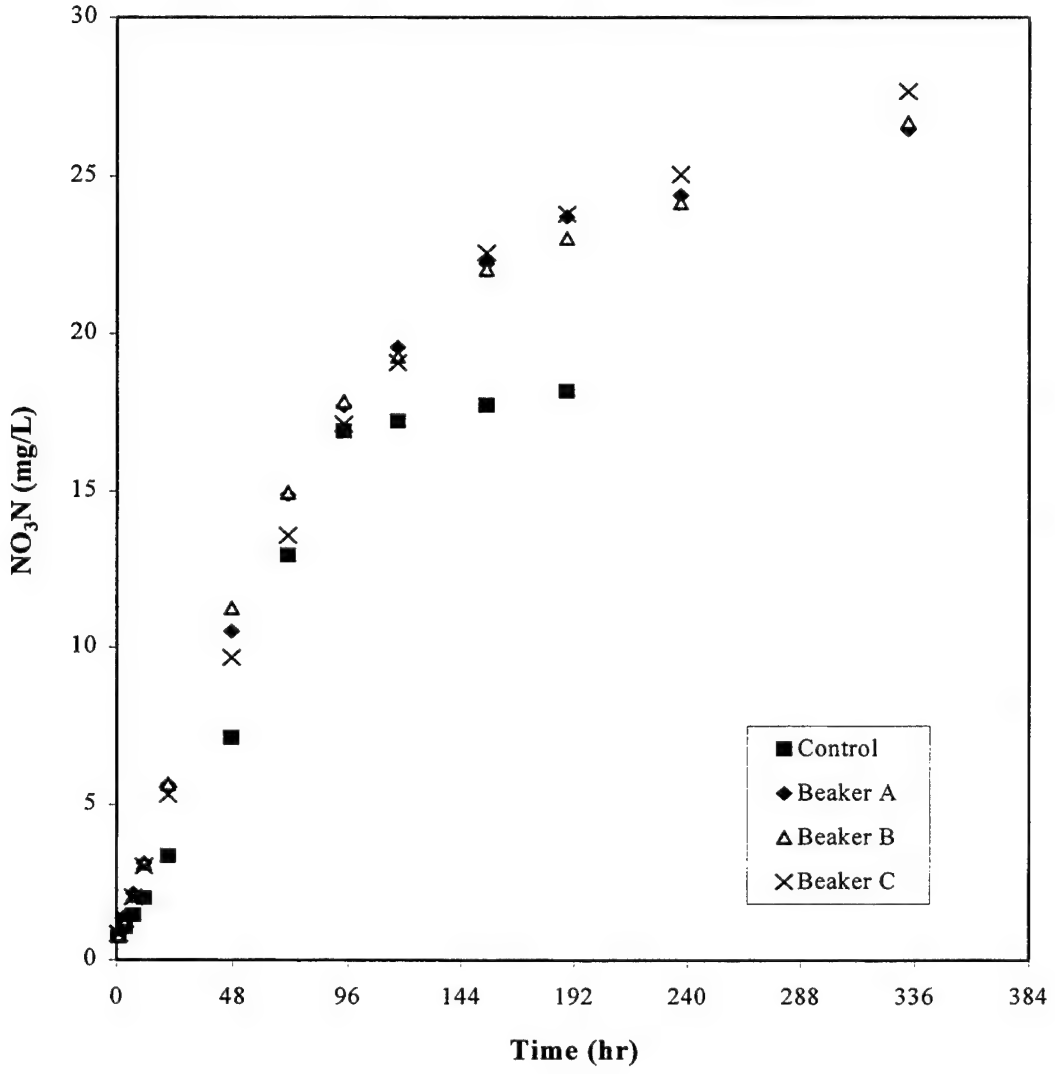

Figure 4.3: Cumulative nitrate production in batch reactors biologically regenerating ammonium-sorbed clinoptilolite (2nd series). The control contains no clinoptilolite.

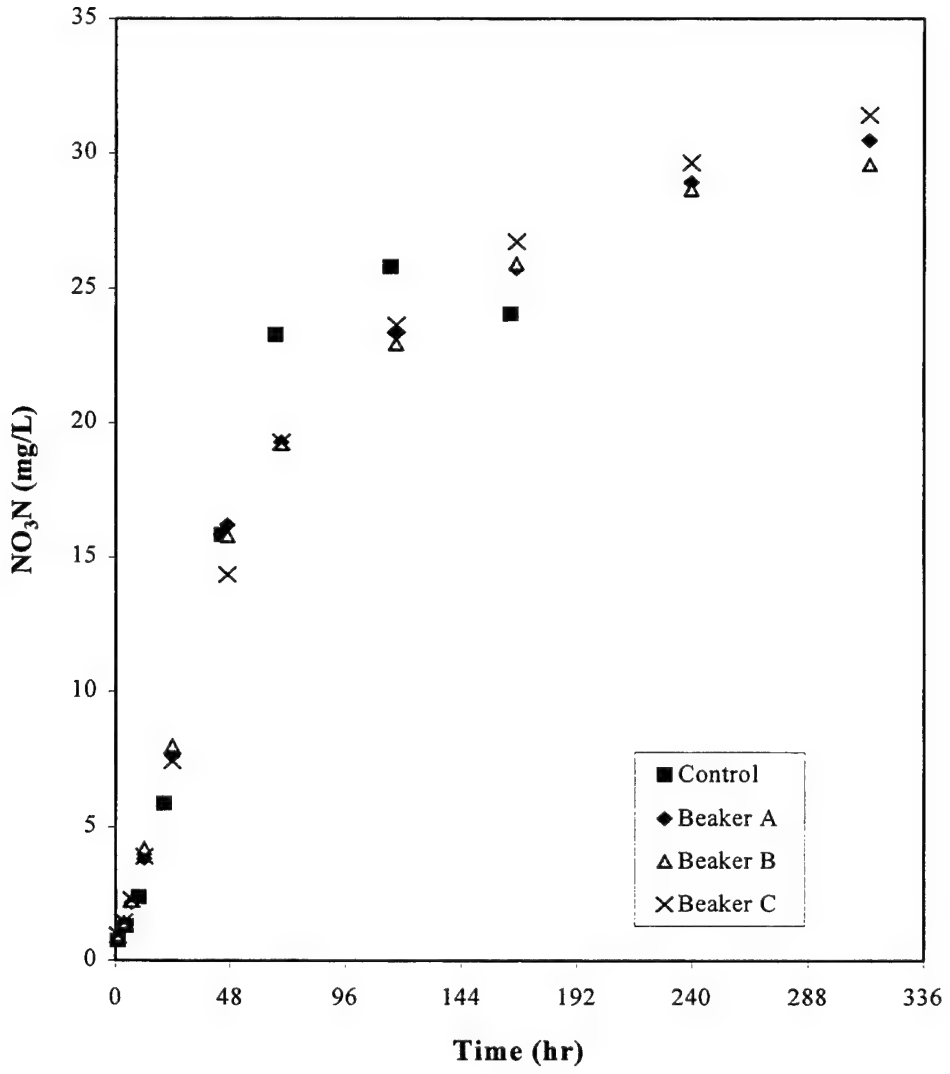

Figure 4.4: Cumulative nitrate production in batch reactors biologically regenerating ammonium-sorbed clinoptilolite (3rd series). The control contains no clinoptilolite.

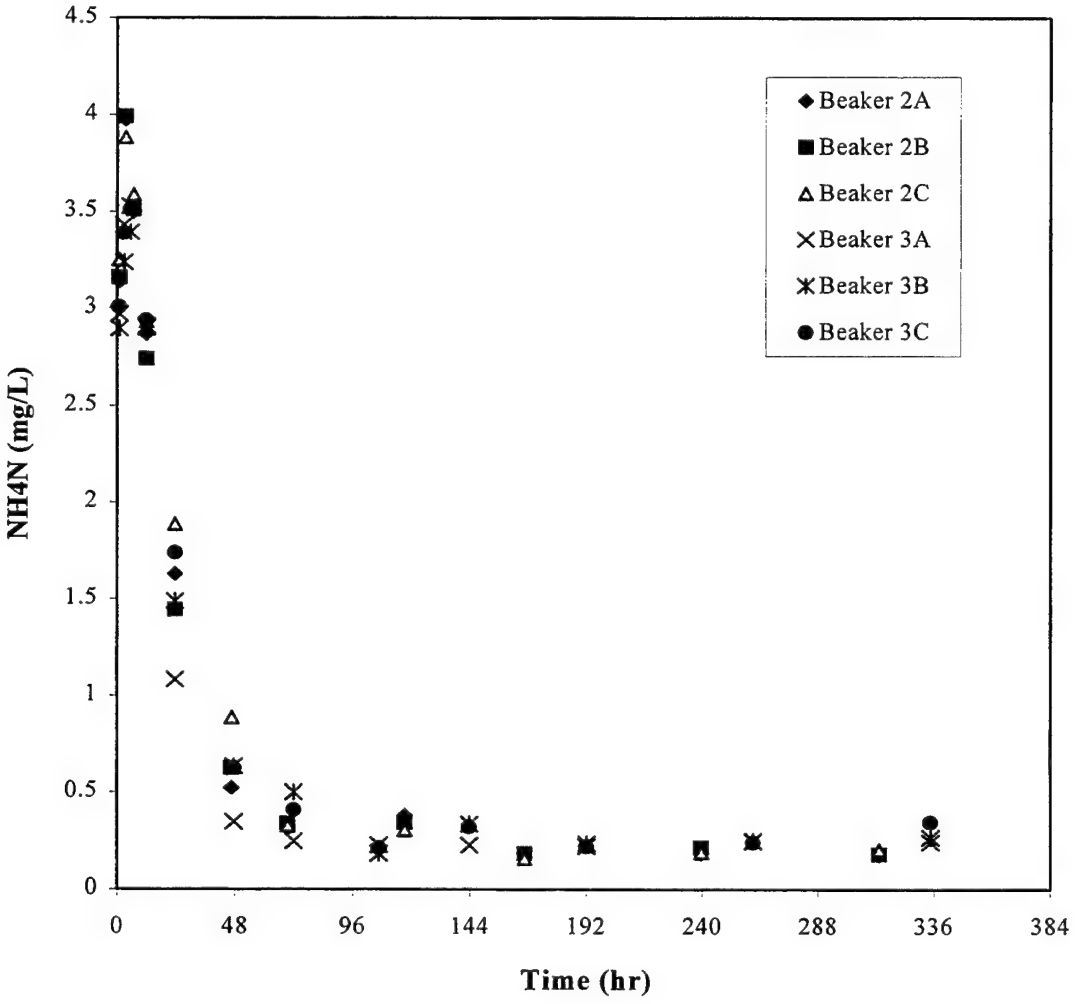

Figure 4.5: Free solution ammonium concentration in beakers A, B, and C for the 2nd and 3rd series of regeneration experiments.

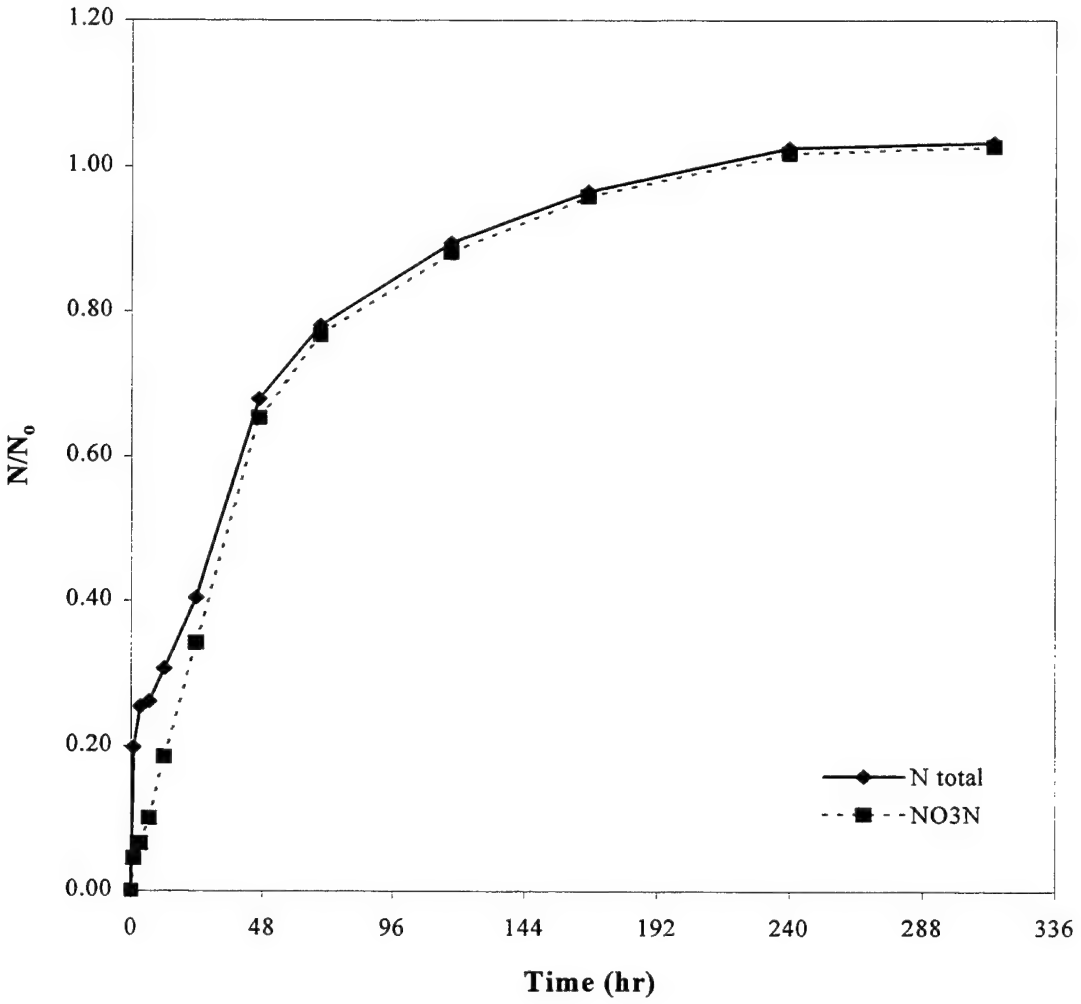

Figure 4.6: Fraction of regeneration based on mass of total nitrogen and nitrate-nitrogen in the free solution in Reactor B (2nd series regeneration).

series of regeneration experiments. The figure shows the difference between the total ammonium eluted and the total ammonium oxidized. After 48 hours, the rate of nitrification equals or exceeds the rate of desorption.

4.2.1.2.2 Regeneration Efficiency

The fraction of regeneration (Figure 4.7) was calculated as:

$$\frac{N}{N_0} = \frac{NO_3N}{NH_4N \text{ initially adsorbed}} \quad \textbf{(4.2)}$$

The fraction of regeneration was based upon total nitrate in the reactor. This is because some of the ammonia data were unusable in the 1st series of experiments due to analytical problems.

There was always a small net production of nitrogen in each of the series of experiments. There are two possible explanations. There were some problems with precipitate formation in the nesslerization technique, which would not effect the nitrate readings, but could influence the adsorption calculations. The nesslerization technique was reevaluated after this series of experiments. EDTA was replaced by Rochelle salt for pretreatment with no further precipitation problems noted. The other possible explanation, and the more likely one, is that the clinoptilolite was not rinsed well enough after the adsorption portion of the experiment which resulted in a slightly higher ammonia solution concentration than what would result if all available ammonium was from desorption.

The fraction regeneration (nitrate production), for all of the data, was modeled using first-order kinetics, which is represented by:

$$\frac{N}{N_o} = 1 - e^{-kt} \quad \textbf{(4.3)}$$

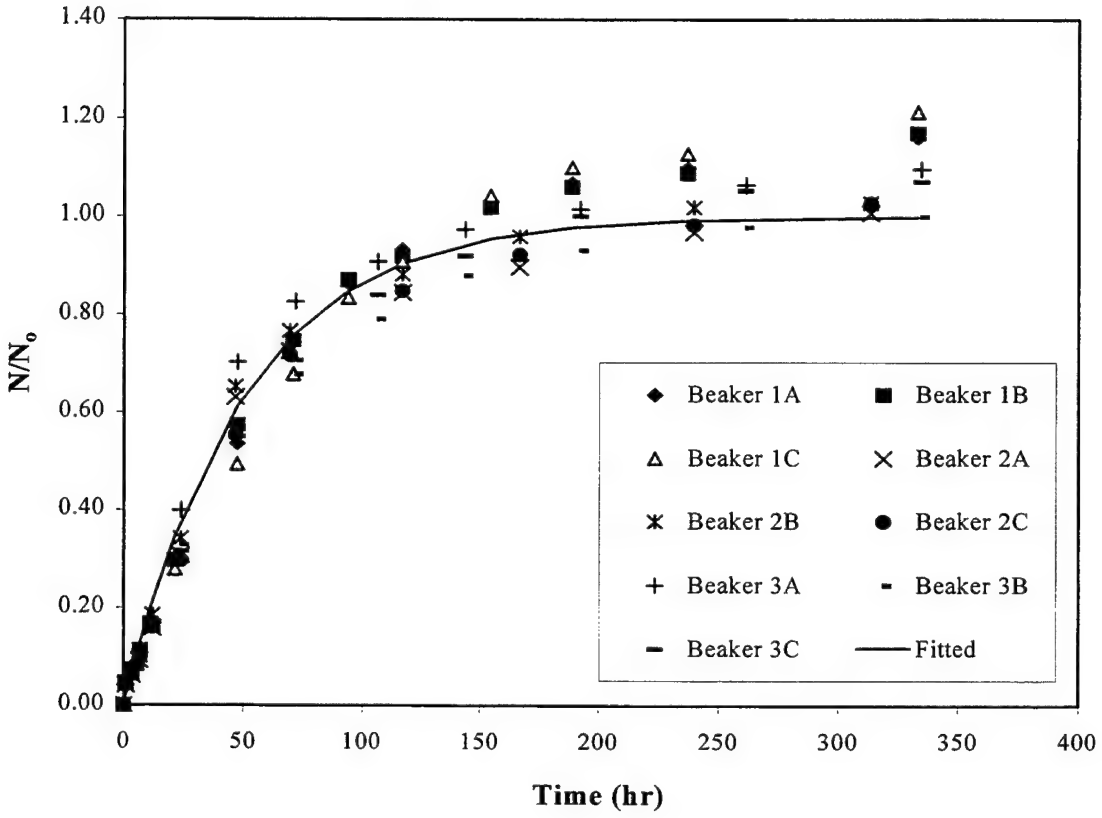

Figure 4.7: Bioregeneration using three reactors (A, B, and C) for three series of regeneration experiments.

The data were fit using the Marquardt-Levenberg nonlinear regression with weighted least squares. N_o was forced to a value of 1.0. The rate coefficient, k was determined to be 0.02 hr^{-1} (See Figure 4.7).

4.2.1.2.3 Nitrification Kinetics

The effect that bulk solution ammonia concentration had on the nitrification rate was investigated (Figure 4.8), and is described using Michaelis-Menten kinetics (eqn 4.4).

$$V_{NO3N} = \frac{V_{max} NH_3N}{K_s + NH_3N} \quad \textbf{(4.4)}$$

Where V_{NO3N} is the nitrification rate at a given ammonia concentration (mg $NO_3N/(L \cdot hr)$), $V_{,max}$ is the maximum nitrification rate (mg $NO_3N/(L \cdot hr)$), K_s is the half substrate rate or the ammonia concentration at $V_{NO3N} = ½ V_{NO3N,max}$ (mg NH_3N/L), and NH_3N is the ammonia concentration in the bulk solution (mg NH_3N/L). For the data set $V_{max} = 0.32$ mg $NO_3N/L \cdot hr$, and $K_s = 0.52$ mg NH_3N/L.

In summary, the batch data show good reproducibility, and the experiments show that it is possible to regenerate ammonium-saturated clinoptilolite with an in-situ nitrifying biomass using tap water as a regenerant. Also, the clinoptilolite can be reused without degrading the adsorptive capacity. These finding reinforce those of Semmens and Goodrich, Jr. (1977) and Semmens *et al.* (1977b).

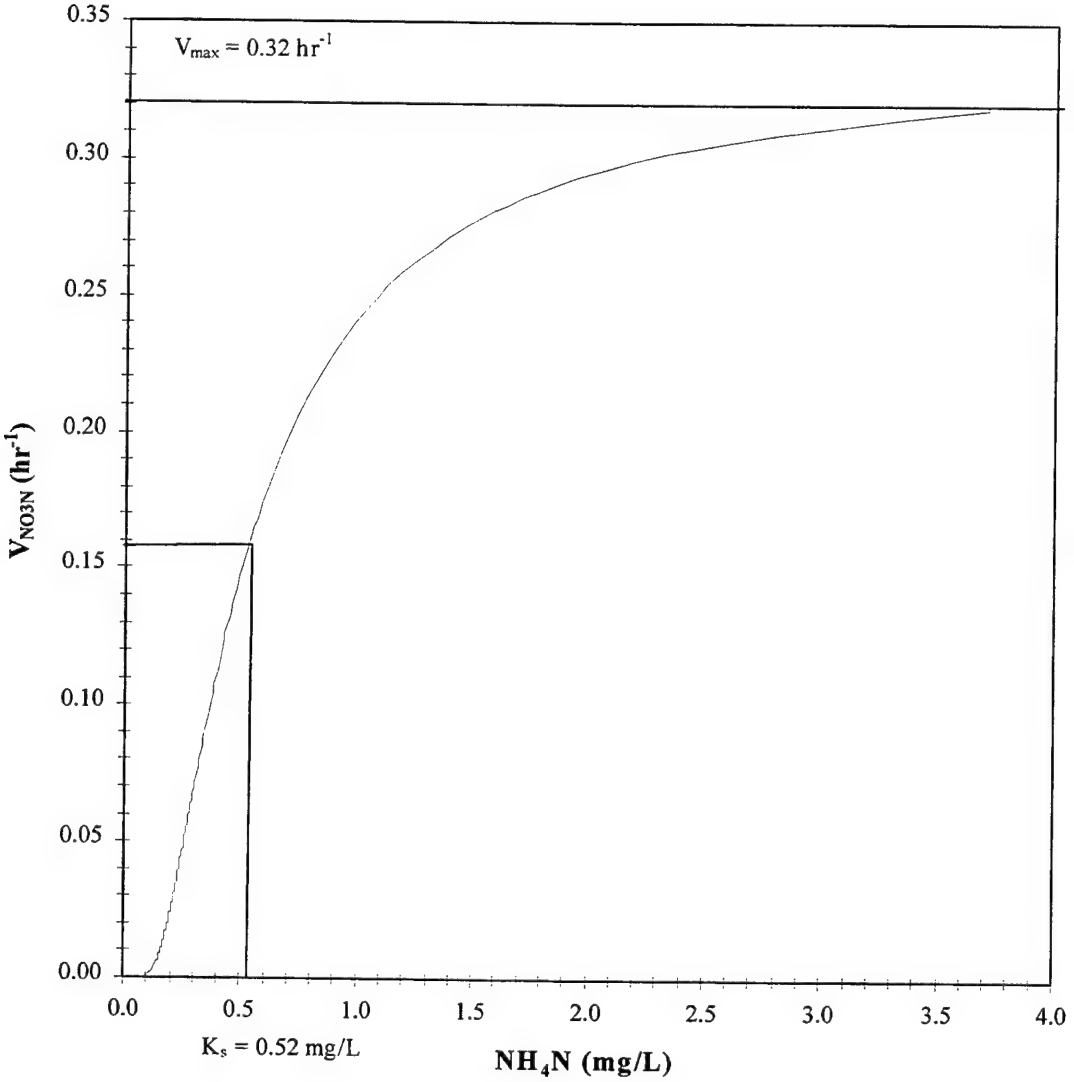

Figure 4.8: Michaelis-Menten representation of nitrification data for batch bioregeneration experiments. The plot was constructed using the best fit curves for the nitrification rate and ammonia concentration data for all three series of experiments.

4.2.1.2.4 Oxygen Requirements

The batch reactors using mechanical stirring were not oxygen limited. DO was measured in each of the four reactors during the first series of regeneration experiments. The DO decreased to 6.6 mg/L after 7 hours in the reactors containing clinoptilolite, and then increased to about 7.9 mg/L after that. DO analysis was abandoned for the batch regeneration experiments based on this finding. Semmens *et al.* (1977b) found that the nitrification rate was a function of the DO at concentrations less than 6 mg/L. Therefore, the nitrification rate was optimized with respect to DO in the batch regeneration experiments, since the DO never dropped below 6.6 mg/L.

4.3 Column Studies - Phase 2

Pilot-scale column studies were the next logical step in the biological regeneration feasibility study. Two studies were conducted. Both used the clinoptilolite as the carrier for the nitrifying biomass. In one column the regenerant was applied down flow in a continuous flow regime. In the other column the regenerant was applied using draw and fill methodology.

4.3.1 Continuous Flow Regeneration

Based on the results of the preliminary studies a clinoptilolite column was constructed with a continuous flow regeneration scheme, an in-situ nitrifying biomass, and in-situ aeration that utilized a perforated PVC diffusor. Three different prototypes of the continuous flow columns were built because of problems that developed after the regeneration experiments were started.

The first column was a complete failure because the mixing caused by the aeration caused the clinoptilolite to migrate through the gravel subbase. The second prototype failed when the filter gasket dislodged during air scouring, even though the system continued to work well. In fact, the 2nd prototype was used for one complete regeneration cycle. However, because of the filter problem, the drainage system was

modified (see Materials and Methods). Three of these 3rd generation prototypes were built.

4.3.1.1 Adsorption Capacity

The three continuous flow columns were connected in series with sampling ports between each column. The purpose was to examine the effect of the loading rate (BV/hr) on the adsorptive capacity with on experiment. A bed volume (BV) for the purposes of this study, is the empty bed volume.

After conditioning, the clinoptilolite was slurried with nitrifying bacteria and deionized water and divided as evenly as possible between the three columns. The BV of each column was calculated based on the height of the clinoptilolite in each column. The volume occupied by the clinoptilolite was 2.5, 2.7, and 2.6 L for column #1, #2, and #3 respectively. The mass of clinoptilolite in each column was estimated by multiplying the total dry mass used for the experiment times the fraction of the total volume found in each reactor. The mass in each column was 2200, 2400, and 2300 g respectively for columns #1, #2, and #3.

Ammonium feed was pumped to the column at a rate of 8.8 L/hr which is 3.5 BV/hr for column #1, 1.7 BV/hr for columns #1 + #2, and 1.1 BV/hr for columns #1 + #2 + #3. The solid-phase concentration in each column was 3.6, 2.7, and 0.4 mg NH_4N/g clinoptilolite in Columns #1, #2 and #3 respectively.

4.3.1.2 Adsorption Breakthrough Curves

Breakthrough curves are shown in Figure 4.9. Originally, breakthrough was set at 2 mg NH_3N/L for column C, however the experiment was stopped early because of clogging problems that could not be alleviated by air scouring. Breakthrough (2 mg NH_3N/L) occurs at 85 BV in column #1 with a loading rate of 3.5 BV/hr; it occurs at 96 BV (#1 and #2), with a loading rate of 1.7 BV/hr. The solid phase concentration (X/m) at breakthrough is estimated to be about 2.4 and 2.8 mg NH_4N/g clinoptilolite for column #1 and #1 + #2 respectively.

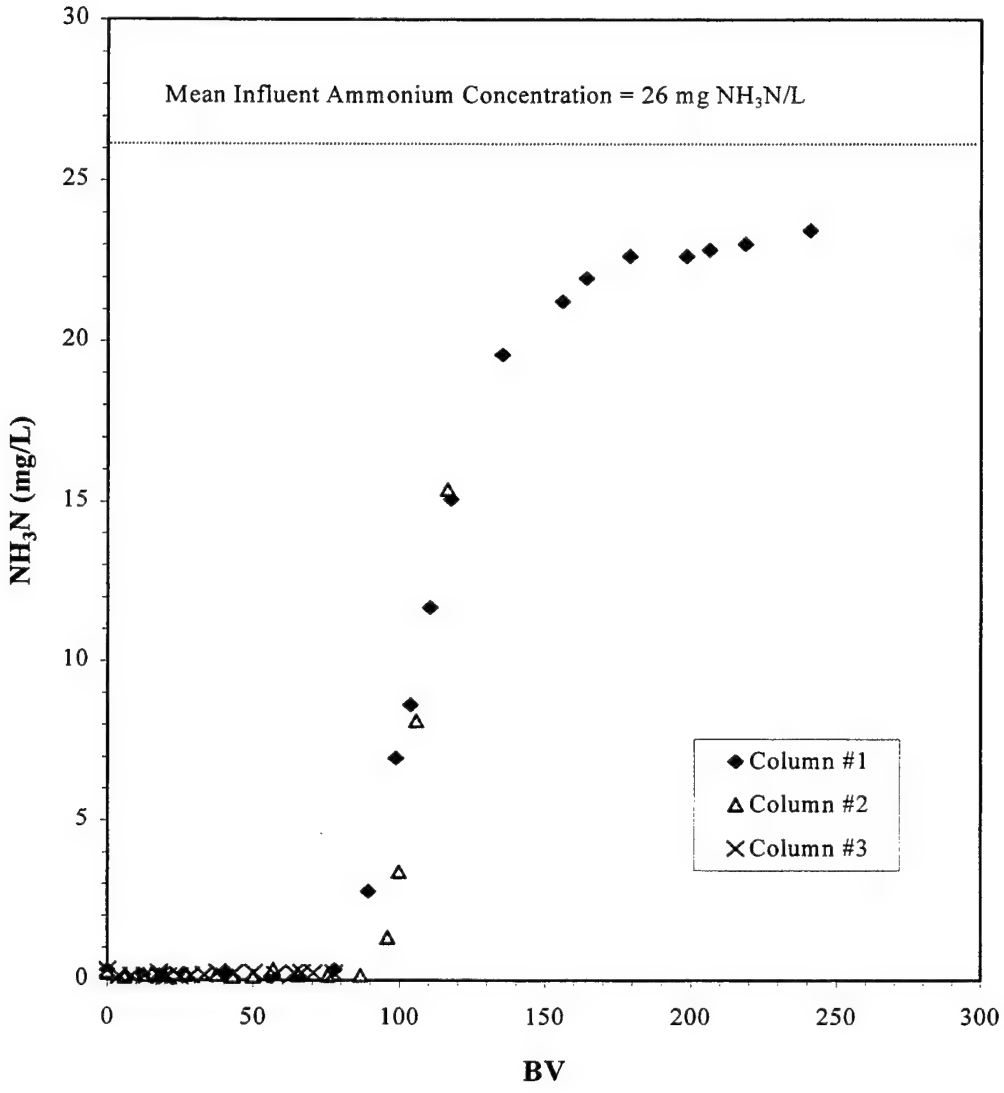

Figure 4.9: Adsorption breakthrough curves for continuous flow clinoptilolite columns at 4°C. The three columns were connected in series.

The relatively steep breakthrough curves are important from a process application perspective, indicating efficient use of the media. Clinoptilolite columns or beds could be used in series or separately with approximately the same results.

The effluent was checked for nitrate production in each reactor approximately half-way through the adsorption experiment. The nitrate concentration was equal to or below that of the feed water. Therefore, nitrification was not occurring in the columns which were at 4°C.

4.3.1.3 Biological Regeneration

4.3.1.3.1 Regeneration Efficiency

Grab samples were used to collect nitrogen and DO data for column #2 and #3. Composite and grab sampling were used to collect nitrogen (NH_3 and NO_3^-) and DO data respectively for column #1. Column #1 and #3 were regenerated at 15°C to simulate worst case process biological regeneration conditions. Column #2 was regenerated at room temperature because of leakage problems. The column was moved to warmer temperatures to fix a leak in the effluent drain. Regeneration was then done at room temperature as a comparison for the cold temperature columns based upon the positive results of column #3.

All data were normalized to BV of regenerant since different loading rates were used for each column. The regeneration rate, on a percentage basis, in all four columns (#1, #2, #3, prototype), is similar for the first 12 to16 BV of regenerant that is applied (Figure 4.10). However, the regeneration rates diverge at this point. The regeneration rate is higher in the prototype column (22°C ±) and column #3 (15°C). The rate of regeneration in column #2 (22°C ±) approaches that of the prototype and column #1 after additional nitrifiers are added to the column. The rate of regeneration in column #1 (15°C) also increases after additional nitrifiers are added, but does not approach that of the other three columns. The presence of nitrifiers may be a key aspect in the regeneration rate of the clinoptilolite.

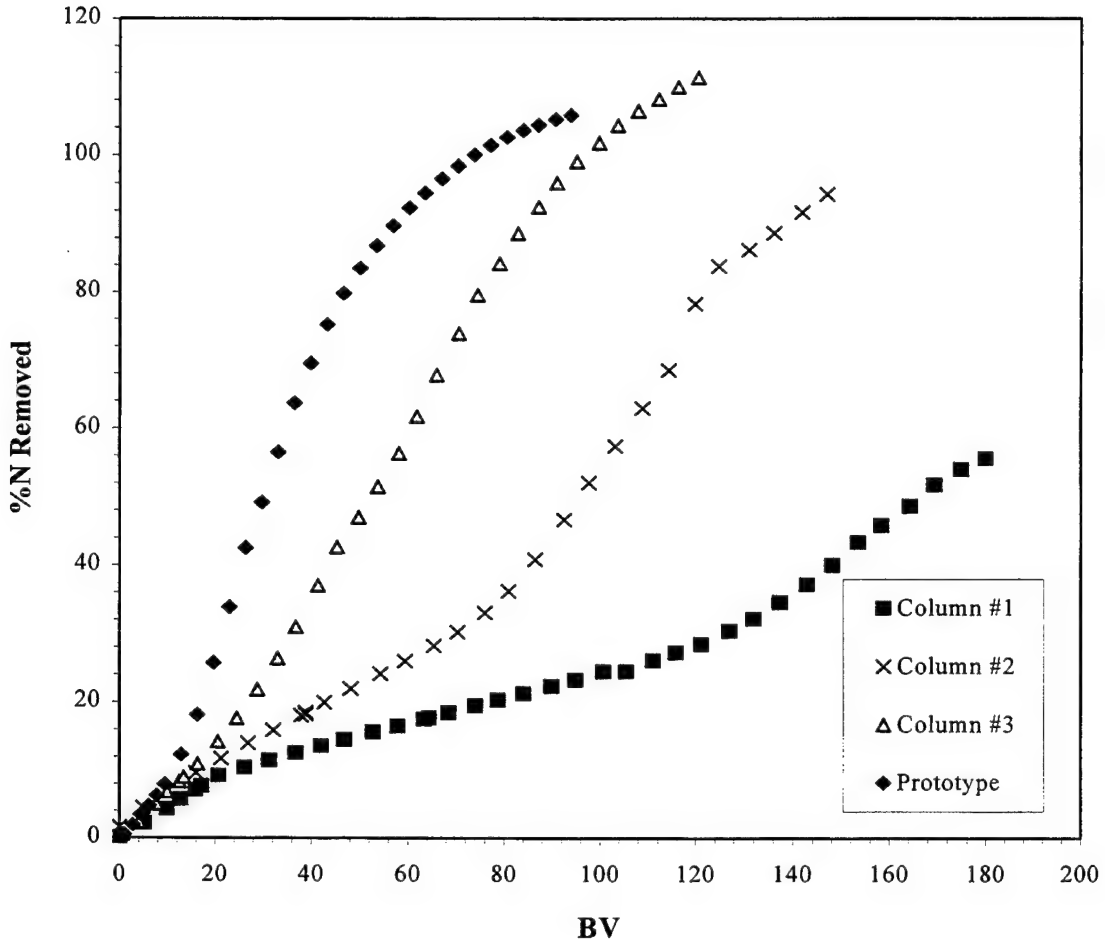

Figure 4.10: Regeneration efficiency for four continuous flow clinoptilolite columns. Column #1 and #3 were regenerated at 15°C, and column #2 and the prototype were regenerated at 22°C. Column #1 had the highest solid-phase concentration while column #3 had the lowest.

4.3.1.3.2 Nitrification Efficiency

The nitrification efficiency in column #3 (Figure 4.11) is much better than that of column #1, #2, and the prototype (Figures 4.12, 4.13, and 4.14). Ammonia accounts for only 4 % of the total nitrogen in the column #3 effluent. Ammonium accounted for 23, 27, and 10 % of the total mass of nitrogen in the effluent from columns #1, #2, and the prototype respectively.

Theoretically, column #1, #2, and the prototype should desorb ammonium at a faster rate because each of these columns had a higher solid-phase ammonium concentration. This is true if you evaluate the total mass of nitrogen removed from each column (Figure 4.15). Columns #1, #2, and the prototype are similarly loaded (X/m = 3.6, 2.7, and 2.5 mg NH_4N/g clinoptilolite respectively), while column #3 has a much lower solid-phase concentration (X/m = 0.4 mg NH_4N/g clinoptilolite). However, the prototype column eventually outpaces both of the higher loaded columns. If the solid-phase concentration is the driving force in desorption then column #1 should be eluting nitrogen at a higher rate than the other two columns. Column #1 actually desorbs at a slower rate than column #2 and the prototype. If the desorption rate limited by the amount of available exchange ions then the hydraulic loading rate of the regenerant is an important consideration.

Column #1 was loaded at the lowest hydraulic rate (4.9 ± 0.8 mL/min), followed by the prototype (5.8 - 6.1 mL/min), column #3 (7.1 ± 0.3 mL/min), and finally column #2 (10.1 ± 0.8). However, the data presented in Figure 4.15 has already been normalized for the total BV of regenerant applied to each column. Therefore, if ammonium desorption from the clinoptilolite is a function of the available exchange ions, then column #2 should be desorbing at the highest rate. In fact, the prototype column desorbed at a higher rate. The nitrifying biomass may play an important role in the desorption kinetics. This hypothesis was investigated in a later controlled batch study and it is also discussed later in this thesis. However, more nitrifiers were added to column #1 and #2 based on this hypothesis, but before the other studies were conducted.

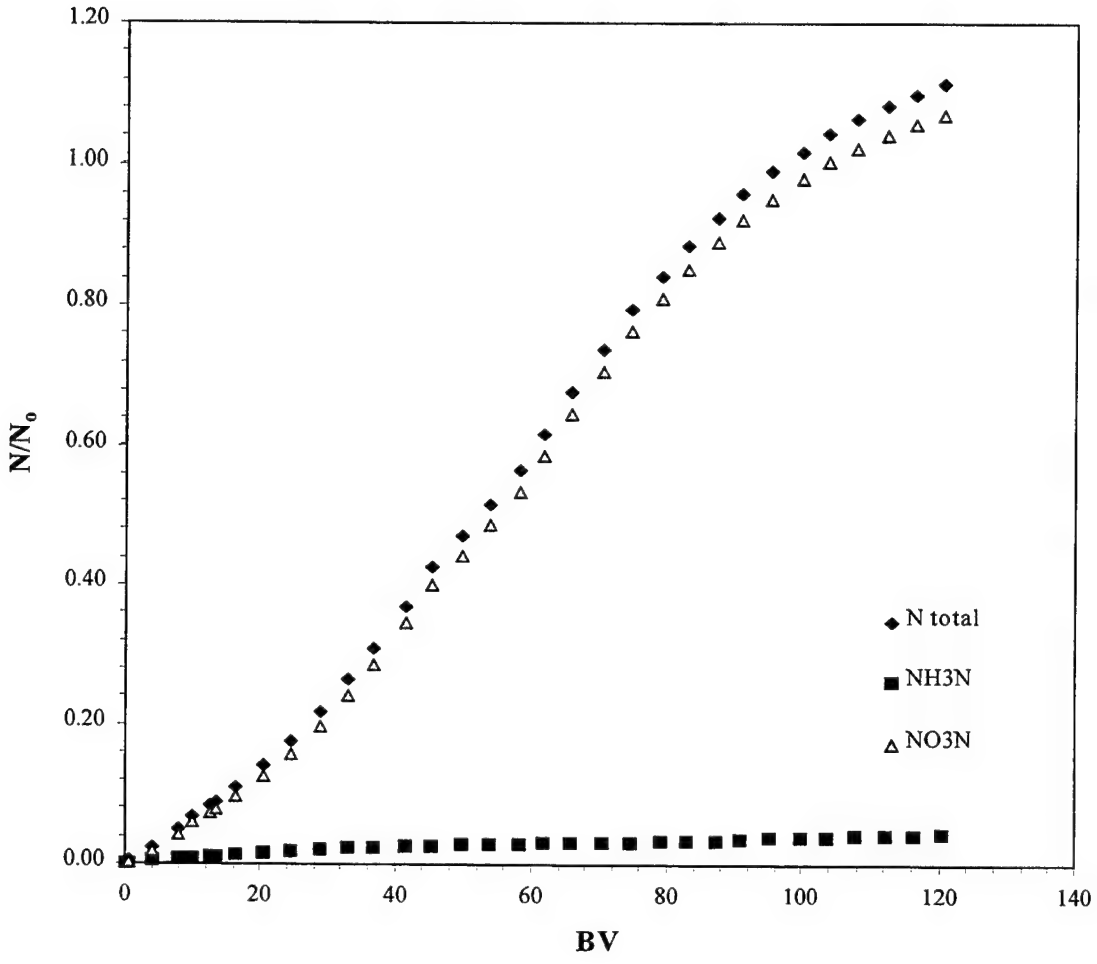

Figure 4.11: Column #3 fraction of regeneration by nitrogen species. The column was regenerated at 15°C. $(X/m)_{initial}$ = 0.39 mg NH_4N/g clinoptilolite.

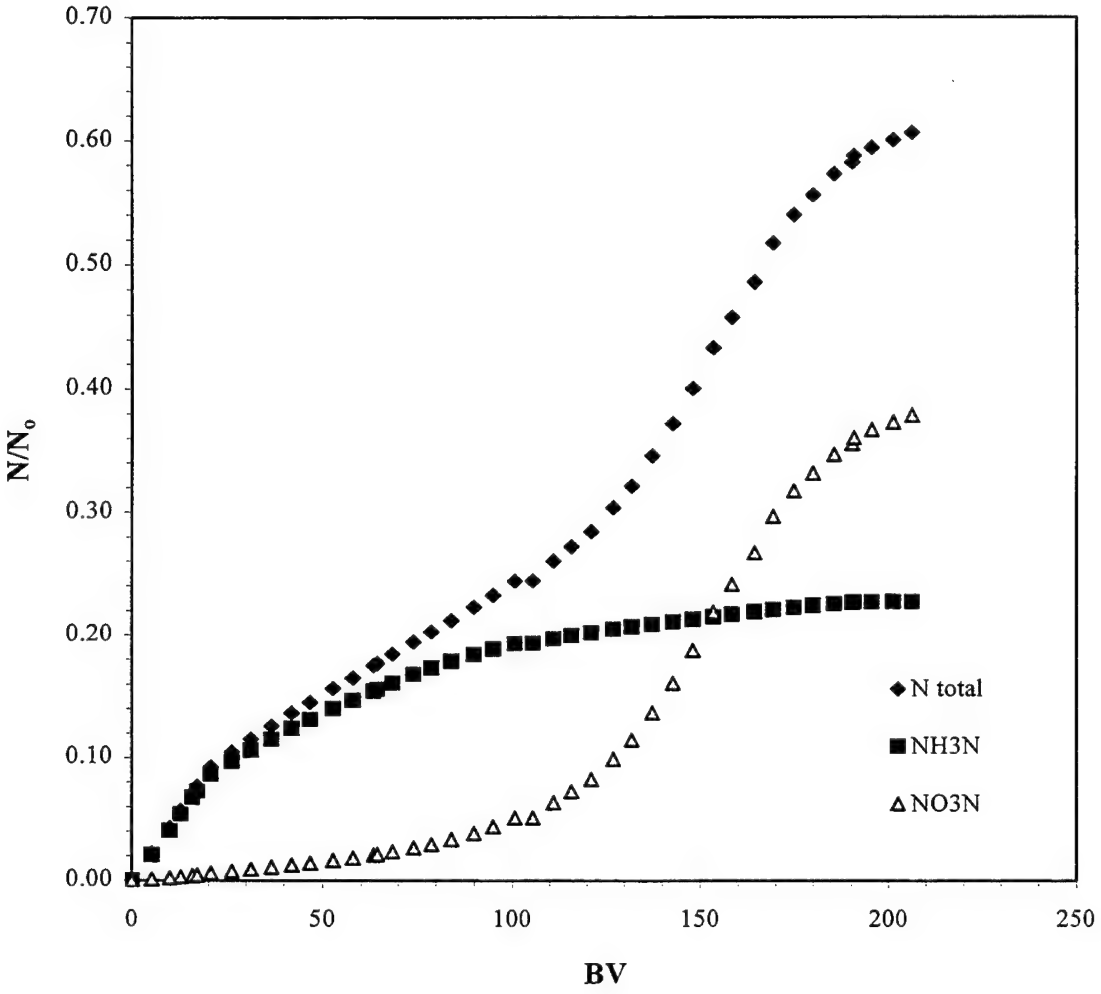

Figure 4.12: Column #1 fraction of regeneration by nitrogen species. The column was regenerated at 15°C. $(X/m)_{initial}$ = 3.6 mg NH_4N/g clinoptilolite.

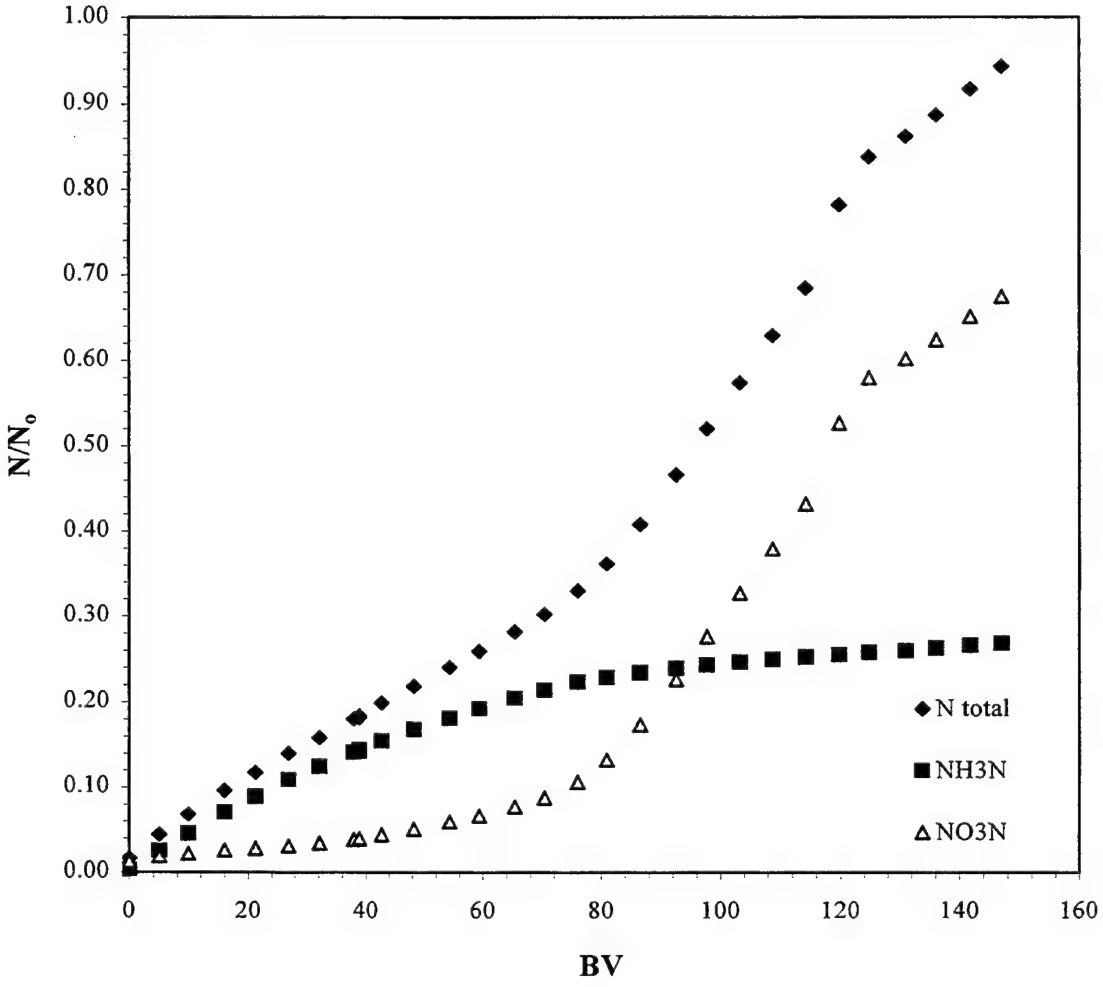

Figure 4.13: Column #2 fraction of regeneration by nitrogen species. The column was regenerated at 22 °C. $(X/m)_{initial}$ = 2.7 mg NH_4N/g clinoptilolite.

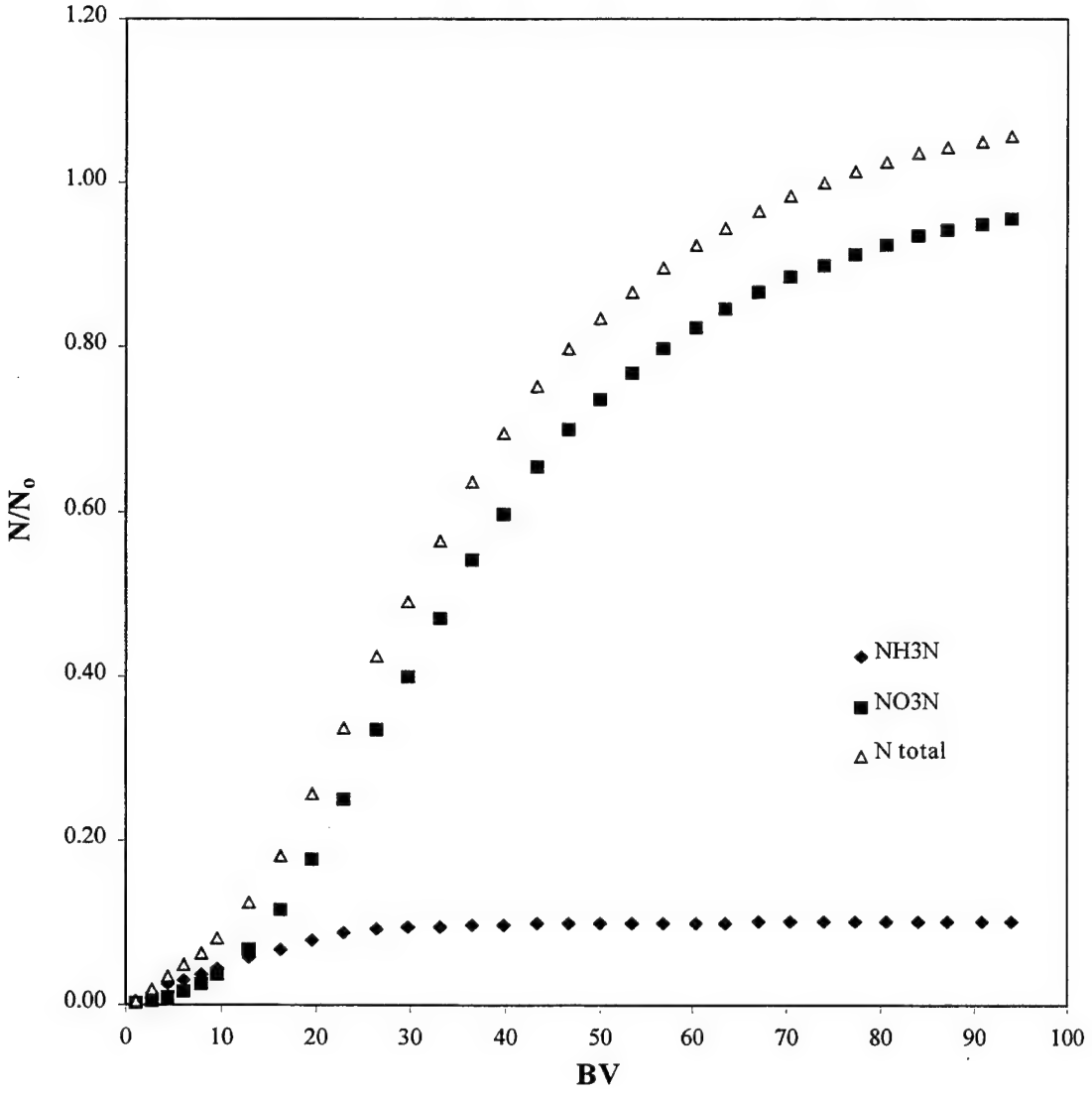

Figure 4.14: Second prototype column fraction of regeneration by nitrogen species. The column was regenerated at 22°C ±. $(X/m)_{initial}$ = 2.5 mg NH_4N/g clinoptilolite.

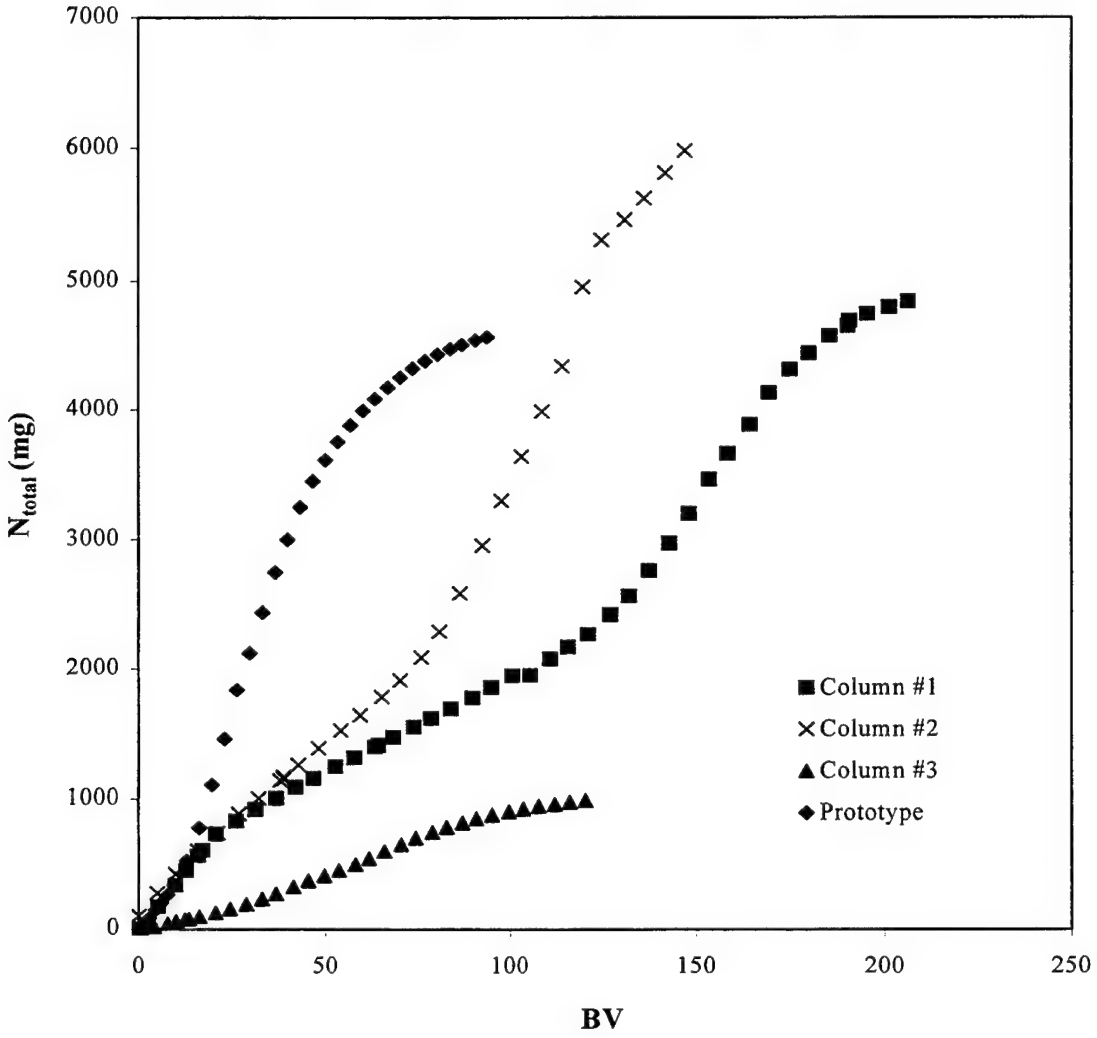

Figure 4.15: Total nitrogen removed from four continuous flow clinoptilolite columns on a mass basis. Additional nitrifiers were added to column #1 and #2 at 60 and 15 BV respectively. $(X/m)_{initial}$ = 3.6, 2.7, 0.4, and 2.5 mg NH_4N/g clinoptilolite for column #1, #2, #3 and the prototype respectively.

The additional nitrifiers were added to column #1 and #2 because the NO_3N concentration was low in column #1 and #2 compared to column #3. After the additional nitrifiers were added to column #1 (@ 60 BV) and #2 (@ 15 BV) the rate of regeneration increased dramatically after a short acclimatization period (Figure 4.17).

Nitrifiers effectively reduce the ammonia concentration in the bulk solution, creating a chemical gradient, which increases the rate of desorption. Even though column #3 was regenerated at a colder temperature than column #2, it was not until after the nitrifiers were added to column #2 that the rate of regeneration, on a percentage basis, matched the rate of regeneration in column #1. In fact, the desorption rate (regeneration rate) increased after the nitrifiers were added to both column #1 and #2 even though the solid phase concentration had decreased in each of the columns.

4.2.1.3.3 Column Failure

Even though biological regeneration of ammonium-saturated clinoptilolite was shown to be feasible, column clogging caused application problems that are difficult to alleviate. The clogging problem was probably cause by the submaximal fluidization induced by the diffusors. Semmens (1978) reported that subfluidizing flowrates cannot be used in a clinoptilolite column or the column would clog; zeolite attrition might be significant under such conditions. All four of the columns produced a significant amount of fine, grayish-white silt. On a volume basis, the total attrition in three of the columns was 8.7, 9.8, and 10.1% for column #1, #2, and #3 respectively. The silt was prevalent in the effluent and would build-up in the effluent plumbing (See Figure 4.16).

Figure 4.16: Silt build-up in column drain line.

Column #1 was removed from service when air scouring would not alleviate the clogging problem. The column was frozen at -20°C and cut in half along the length of the column. There was a significant zone of compressed material that had

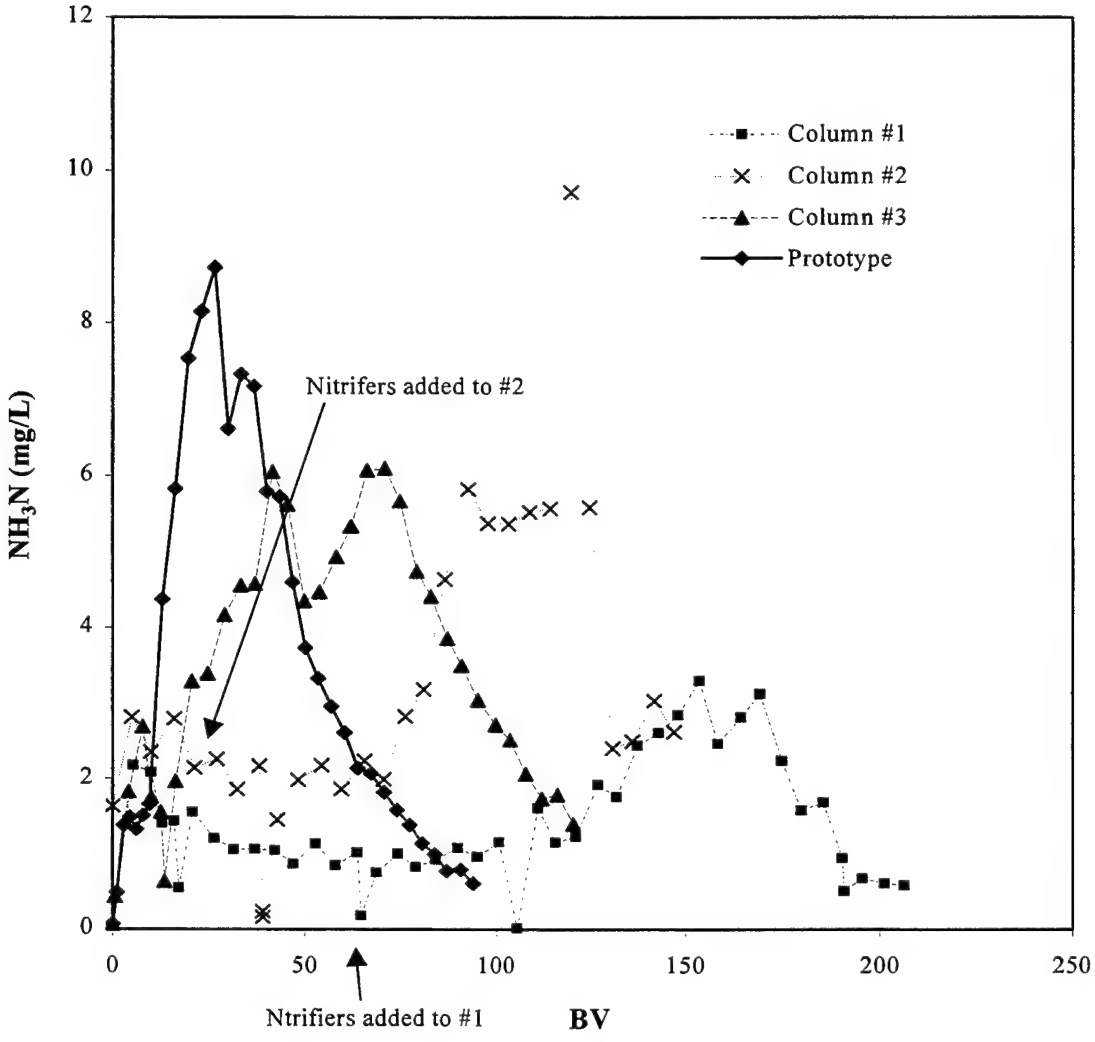

Figure 4.17: Total ammonia desorbed from continuous flow bioregeneration columns. The ammonia is the sum of the nitrate and ammonia in the effluent.

formed just above air diffusor (Figure 4.18). It is believed that this zone of compression continued to migrate down through the column until it completely compacted the area surrounding the effluent drain line.

Clogging in column #2 was so severe that it was removed from service early in the regeneration process. The water inside of the column could not be drawn through the drain line with a vacuum. At this point, the contents of column #2 were dumped into a large bucket, and washed with deionized water to remove any fines. Upon inspection, it was discovered that there was a significant amount of compaction just below the air diffusor. The compacted clinoptilolite in the bottom of the column could only be removed by breaking it up with a stick. The clinoptilolite was dumped back into the column and regeneration operations were continued. The column clogged again later, but only after it had been almost completely regenerated.

Based on these findings the continuous flow, the in-situ nitrification and aeration regeneration process was abandoned.

4.3.2 Draw and Fill Regeneration

In-situ nitrification utilizing passive aeration with draw and fill regenerant application was investigated as an alternative method of biological regeneration. Two columns were used in this study. One was built with 1.25" ID acrylic tubing (column A), and the other was built with 1" ID PVC (column B). Column A was regenerated at 14°C while column B was regenerated at 20°C ±.

4.3.2.1 Adsorption

There is little difference in the breakthrough curves even though column A was loaded at twice the hydraulic loading rate as column B (Figure 4.19). The total adsorption in column A was 825 mg NH_4N resulting in a solid-phase NH_4N concentration of 3.30 mg/g clinoptilolite (0.24 meq/g) at an effluent ammonia concentration of 18 mg NH_3N/L. The effluent ammonia concentration was allowed to exceed the predetermined breakthrough concentration (2 mg NH_4N/L) in order to investigate the effect of heavy

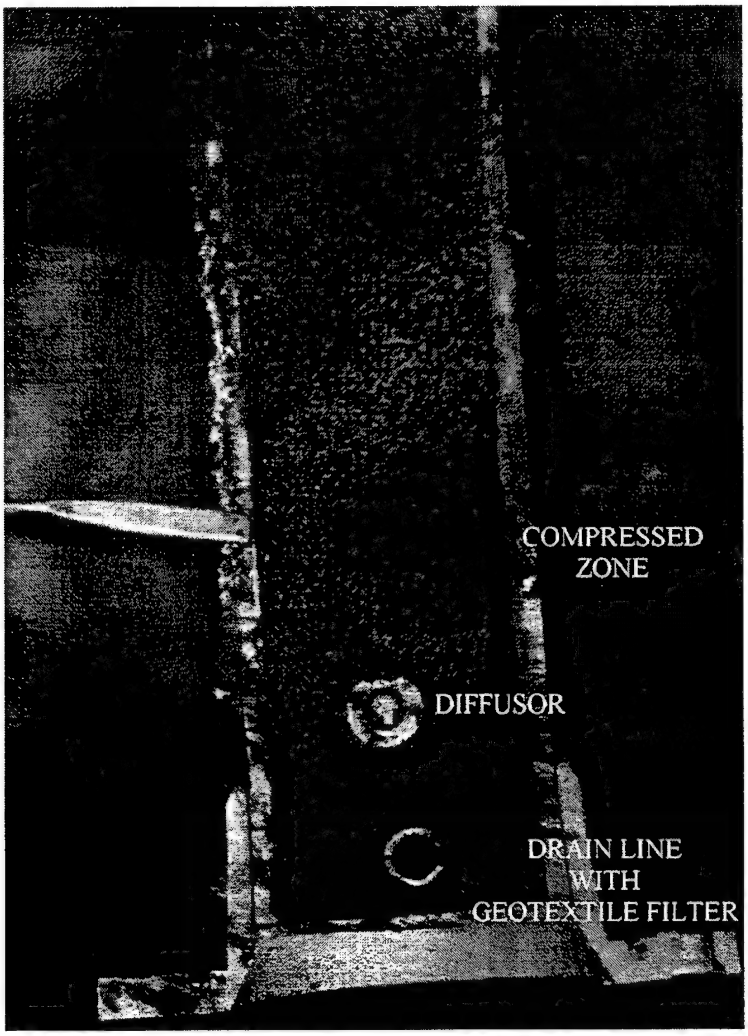

Figure 4.18: Compressed zone of fine clinoptilolite caused by submaximal fluidization.

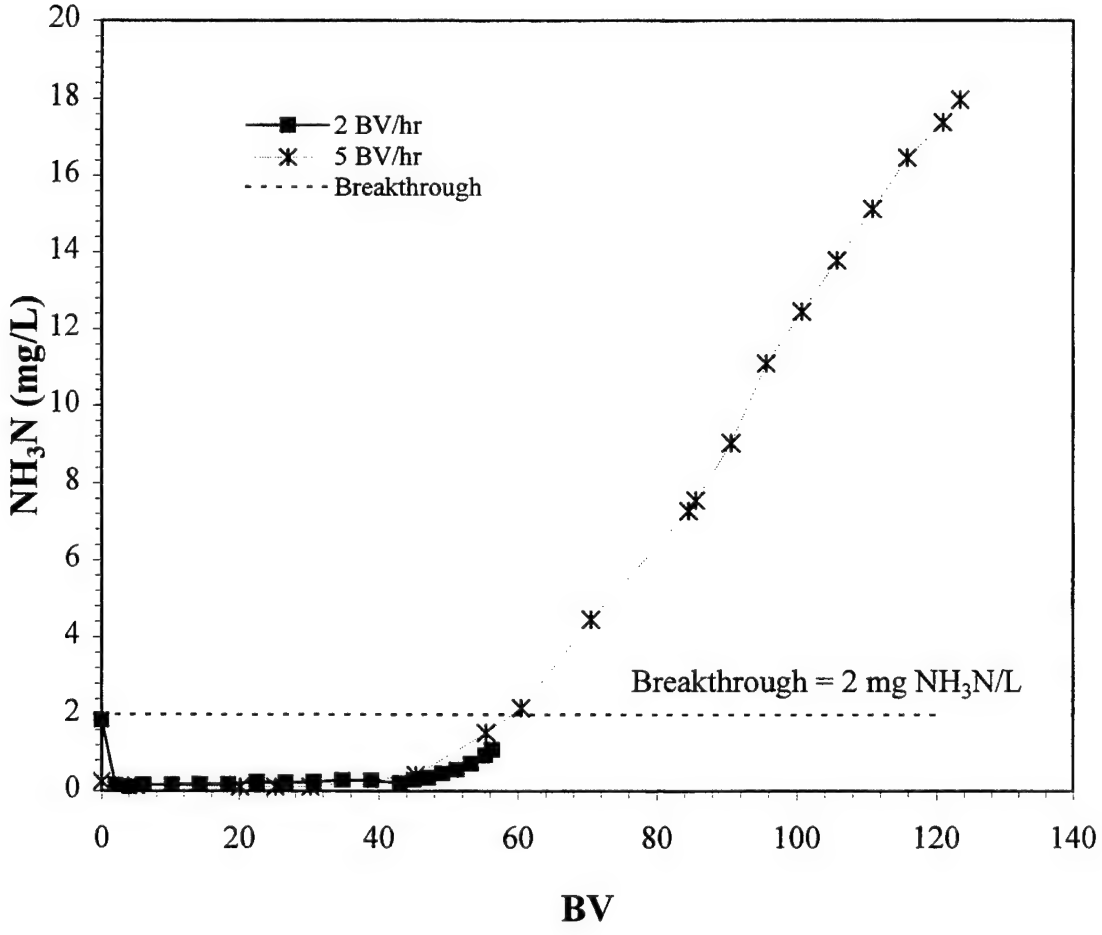

Figure 4.19: Adsorption breakthrough curves for draw and fill clinoptilolite columns. Average influent NH_3N concentration = 26 mg/L (T = 4°C). Column A was loaded at 5 BV/hr and column B was loaded at 2 BV/hr.

loading on regeneration. At breakthrough the total adsorption capacity was 2.0 mg NH_4N/g clinoptilolite at 59 empty bed volumes (BV).

The total adsorption in column B was 478 mg NH_4N for a solid concentration of 1.9 mg NH_4N/g clinoptilolite (0.14 meq/g) at an effluent ammonia concentration of 1.1 mg NH_3N/L. It was estimated that breakthrough would have occurred at approximately 64 BV.

4.3.2.2 Bioregeneration

4.3.2.2.1 Data Normalization and Assumptions

The data were normalized to BV because different cycling rates were used throughout the bioregeneration experiments for both column A and column B. A mass-balance approach (NH_4N, NH_3N, NO_3N, and NO_2N) was used to calculate the fraction of NH_4N removed from the column.

Ammonia volatilization was assumed to be zero. The effluent pH and ammonium/ammonia concentration were both low. Based on this, the actual ammonia concentration in the effluent was at or near zero.

4.3.2.2.2 Bioregeneration Efficiency

It is possible to biologically regenerate ammonium-sorbed clinoptilolite with tap water and nitrifying bacteria (Figure 4.20). Assuming a target of 90% regeneration, it took 80 BV and 37 BV to reach 90% regeneration in column A and B respectively. The rate of regeneration, expressed as the percent of ammonium initially adsorbed, was higher in column B than in column A. This is because the total amount of ammonium initially sorbed to column A is higher than that in column B. Theoretically, the more readily accessible exchange sites in the clinoptilolite will adsorb the ammonium, and therefore should also more readily desorb the ammonium. On a mass basis, the ammonium desorption rate from both columns is similar (Figure 4.21). However, the form of nitrogen found in the effluent was different for each column.

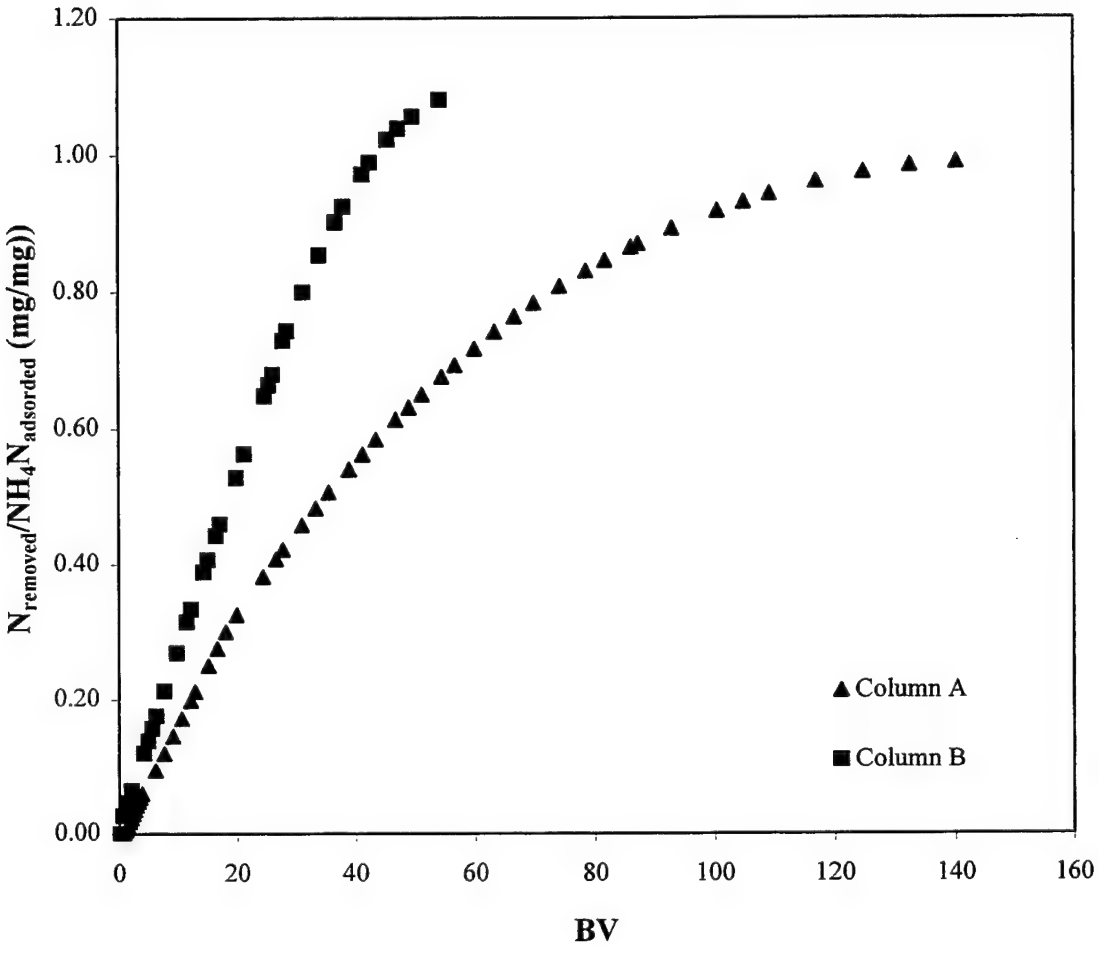

Figure 4.20: Regeneration efficiency based on the total NH4N originally adsorbed in each column. $NH_4N_{adsorbed,A}$ = 825 mg, T_{regen} = 14°C; $NH_4N_{adsorbed,B}$ = 478 mg, T_{regen} = 20°C.

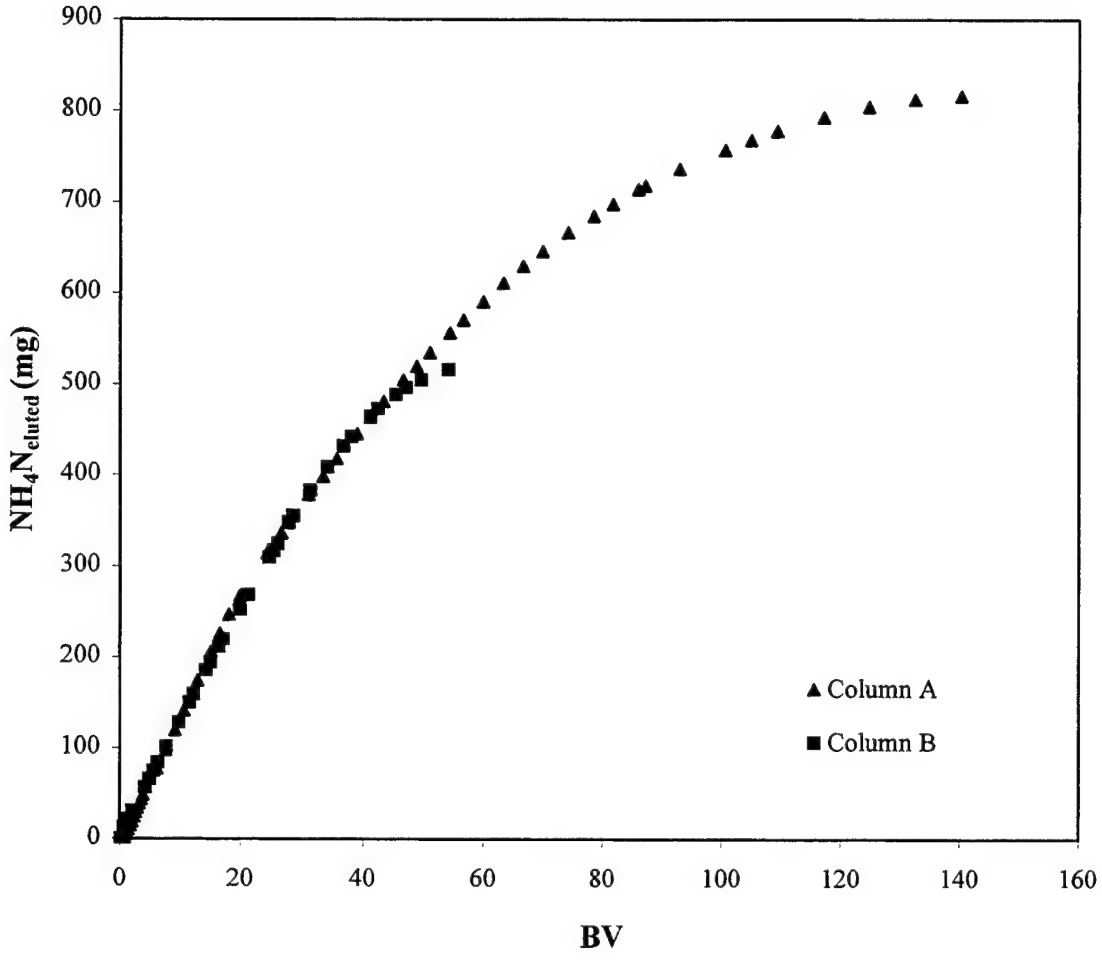

Figure 4.21: Total ammonium eluted from the clinoptilolite column as total nitrogen (NH_4N, NH_3N, NO_3N, NO_2N).

4.3.2.2.3 Ammonium, Nitrate, and Nitrite

The effluent ammonia concentration was much higher in column A (Figure 4.22). A higher effluent ammonia concentration would be expected in column A since the solid-phase ammonium concentration is much higher (3.1 mg NH4N /g clinoptilolite versus 1.9 mg NH4N /g clinoptilolite). However, the bioregeneration temperature in column A was lower, therefore, the nitrifying bacteria could not oxidize the ammonia as efficiently as they would in column B.

The nitrate concentrations (Figure 4.23) were similar in both columns during the initial stages of regeneration (< 40 BV). However, the nitrate concentration in column B drops off quickly after this point which is probably due to the decrease in available sorbed ammonium, since the nitrification efficiency was approximately 99%. Throughout both experiments the effluent nitrite concentrations were less than 0.1mg/L.

4.3.2.2.4 Nitrification Kinetics

During the initial stages of regeneration the nitrification rate (V_{NO3}) in both column A and column B are similar. The maximum nitrification rate is slightly higher in column A than it is in column B even though column A was regenerated at a lower temperature. The nitrifiers had more time (an additional 12 hours) to oxidize the ammonia in column A initially because the regenerant was applied at one cycle/d. Even when regenerant was applied at 2 cycle/d the nitrification rate was higher in column A than it is in column B. This was probably due to the fact that the solid phase concentration in column A is higher than that of column B.

The nitrification efficiency was 87% efficient in column A during the first 10 days of regeneration, but increased to an overall efficiency of 94%. The nitrification efficiency for column B was 99%, based on the total ammonium desorbed from the clinoptilolite. The rate of desorption exceeds the rate of nitrification initially in both columns, but after a period of acclimatization (< 2 d) the nitrifiers in column B do a much better job of ammonia oxidation. The difference between the two columns is probably caused by the temperature difference.

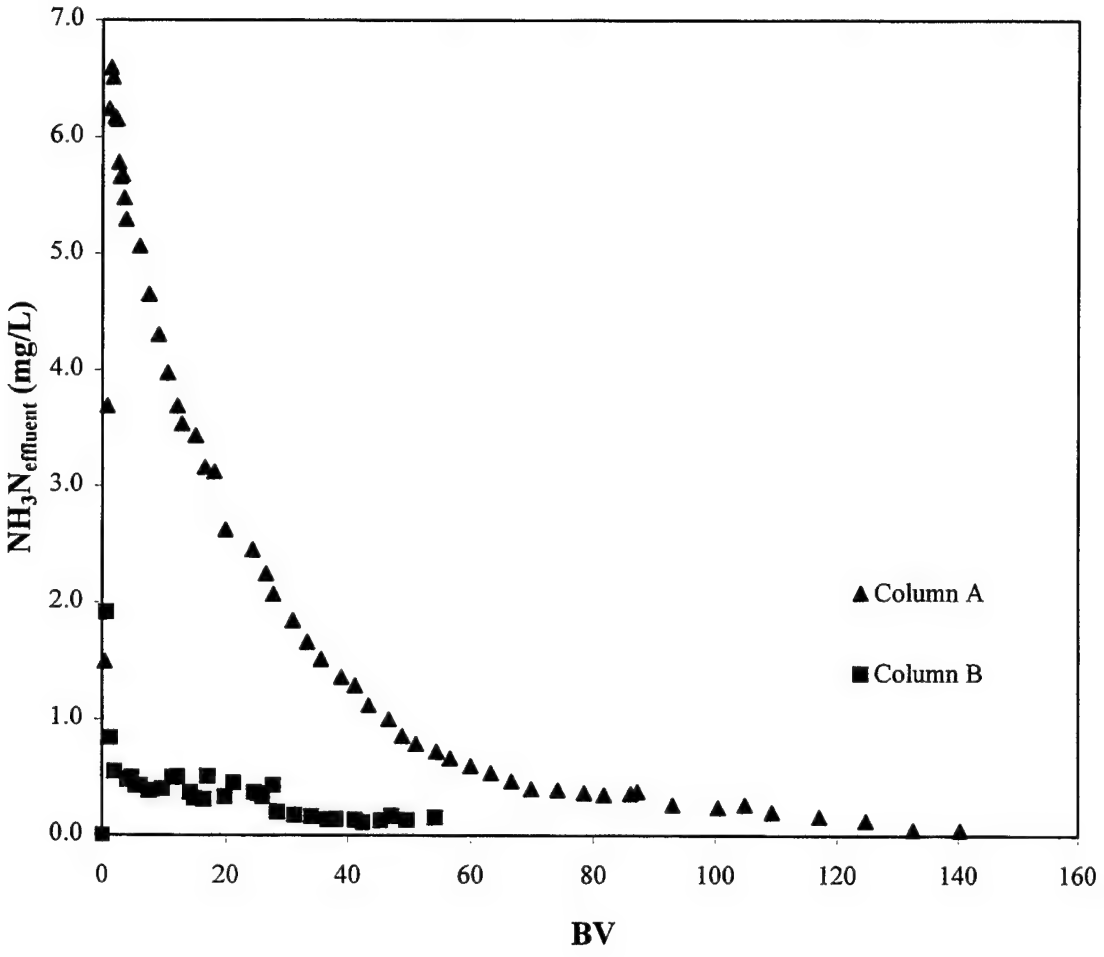

Figure 4.22: Effluent ammonia concentration in draw and fill clinoptilolite columns.

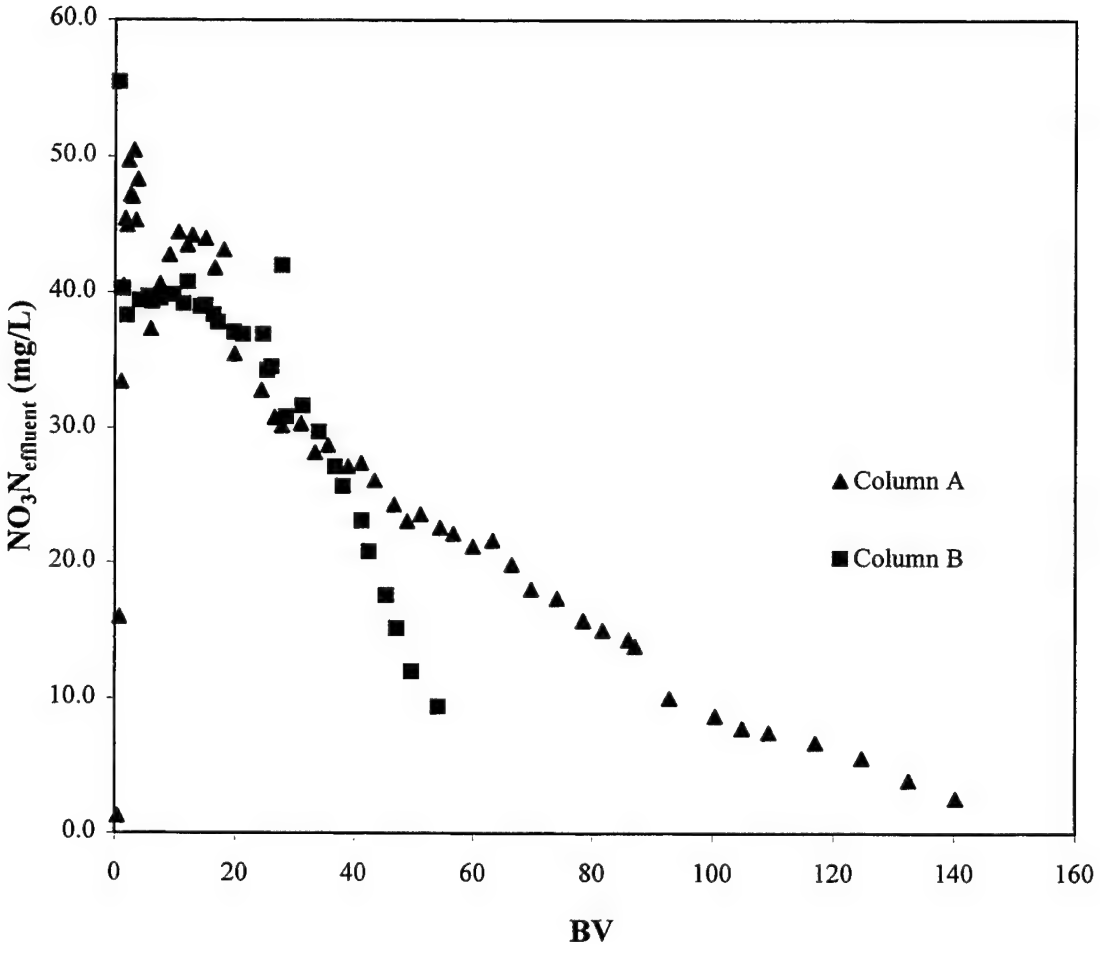

Figure 4.23: Effluent nitrate concentration in draw and fill clinoptilolite columns.

The nitrification rate was modeled by Michaelis-Menten kinetics (Figure 4.24). V_{max} = 16.5 and 19.0 mg NO_3N/BV, and K_s = 1.0 and 0.2 mg NH_3N/L for column A and B respectively. The parameters obtained for column B may not be as accurate since the nitrifiers are essentially operating in the linear portion of the Michaelis-Menten curve.

4.3.2.2.5 Alkalinity

Based on theoretical requirements (7.14 mg alkalinity as $CaCO_3 \cdot mg^{-1}$ NO_3N produced), there was not enough alkalinity present in the feed water to produce the effluent nitrate in column A or B. The feed had an alkalinity concentration of 255 $mg \cdot L^{-1}$ as $CaCO_3$ with a pH of 8.66. Alkalinity requirements were as high as 400 $mg \cdot L^{-1}$ as $CaCO_3$ (Figure 4.25), but the effluent pH never dropped below 6.6. The clinoptilolite may have some type of buffering capacity. It may be adsorbing protons from the bulk solution and exchanging them with ammonium ions when there are not enough other counter ions available. This subject needs further research.

4.3.2.2.6 Oxygen Requirements

The draw and fill aeration column system is very efficient when it comes to using the available oxygen in the pore spaces. Based on the total mass of ammonium that adsorbed to each column, it should take 43 BV and 24 BV of regenerant to oxidize the total ammonium in column A and B respectively (0.27 mg O_2/mL of air). It actually took 37 BV to reach 90% regeneration in each column. During the initial stages of regeneration ($NO_3N_{effluent}$ = 40 mg/L) the nitrifying biomass utilized 68% of the available oxygen. Oxygen use efficiency was as high as 95%.

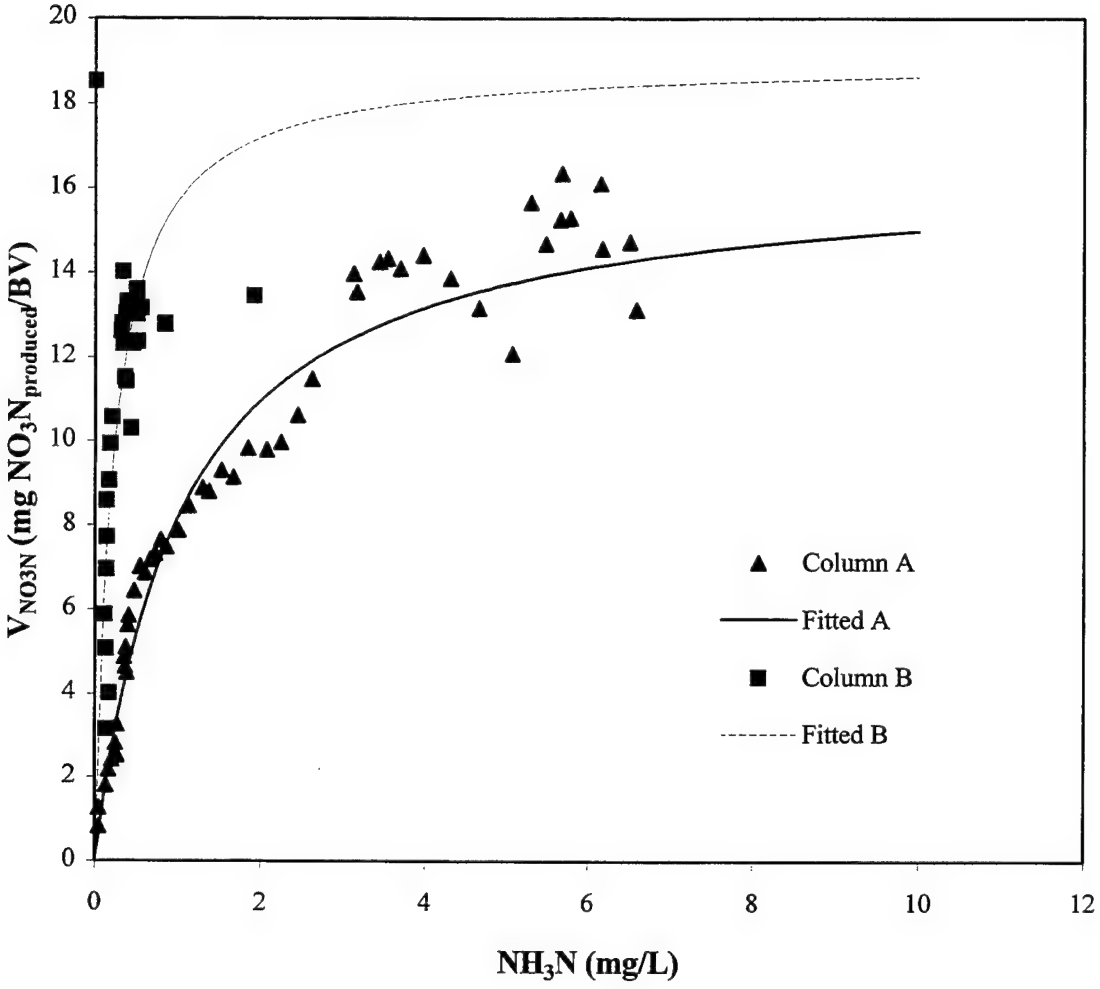

Figure 4.24: Nitrification rate. Curve fitting using Marquardt-Levenberg algorithm. V_{max} = 16.5 and 19.0 mg NO_3N/BV, and K_s = 1.0 and 0.2 mg NH_3N/L for column A and B respectively.

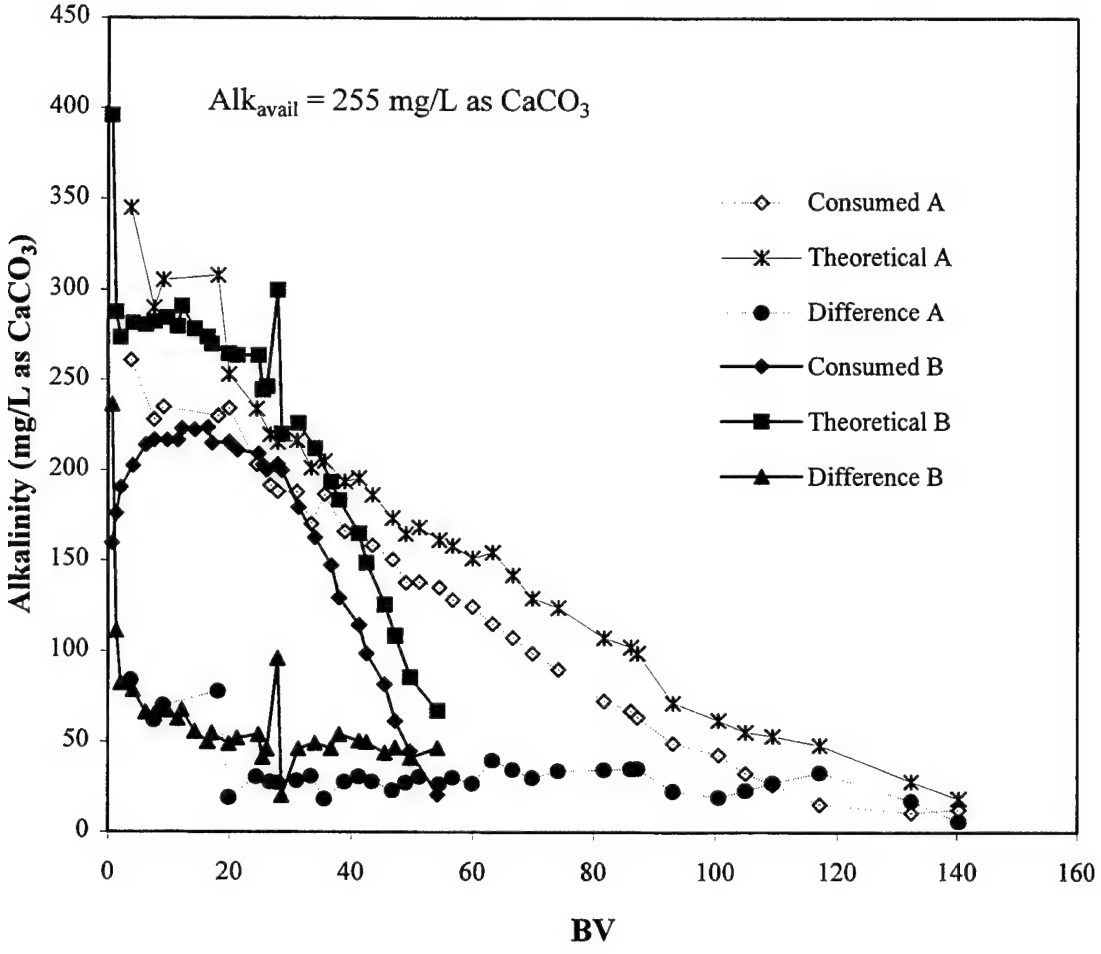

Figure 4.25: Alkalinity consumed. Theoretical based upon 7.14 mg $CaCO_3$/mg NO_3N produced.

4.3.3 Laboratory-Scale Experiments and the Presence of Nitrifiers

Two laboratory-scale experiments were used to look at the influence of the nitrifying biomass on the regeneration of ammonium-sorbed clinoptilolite. The purpose of the first experiment was to examine the effect of nitrifier concentration on the rate of regeneration. The second laboratory-scale batch experiment was conducted to see what effect the presence of nitrifiers had on the regeneration rate using tap water and deionized water.

4.3.3.1 Batch Nitrifier Experiment #1

In the first laboratory-scale experiment which used tap water as a regenerant, the rate of regeneration was 180 % (flask C) and 190 % (flask B) faster than in the flask without nitrifiers (flask A) (Figure 4.26). No conclusion can be drawn as to the influence of the nitrifier concentration on the regeneration rate, since the regeneration rates were similar in both of the flasks that had nitrifiers. Further study is needed, but it may not be that important since there are no plans to control nitrifier growth on the clinoptilolite media.

Ammonia was the main constituent of the effluent in flask A (95 ± 1%). In the other flasks, the percentage of ammonia in the effluent decreased during the experiment. It ranged from 61 - 36% and 63 - 30% in flasks B and C respectively. The nitrification efficiency stabilized after approximately 2 days in both flasks B and C at 66% and 68% respectively (Figure 4.27).

4.3.3.2 Batch Nitrifier Experiment #2

The presence of nitrifiers had a more profound impact in the second laboratory-scale study. The rate of regeneration was 380% higher in flask B (tap water, no nitrifiers) than it was in flask A (deionized water) (Figure 4.28). It was 480% higher in flask C (deionized water, nitrifiers), and 1340% higher in flask D (tap water, nitrifiers)

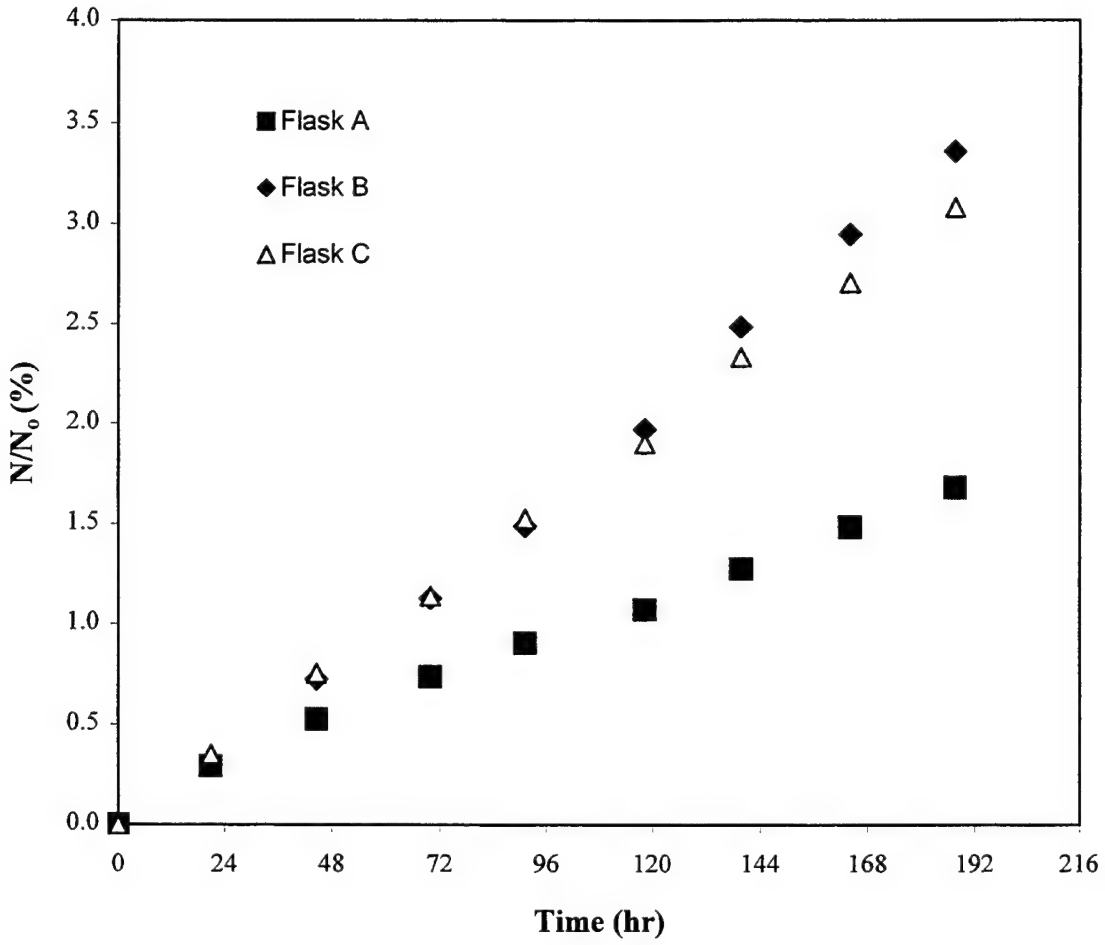

Figure 4.26: Regeneration efficiency for batch draw and fill experiment #1. Regeneration temperature = 15 °C. Flask A contains no nitrifiers. Flask B and C were seed with 30 mL and 90 mL of washed nitrifiers respectively. Tap water was used as a regenerant.

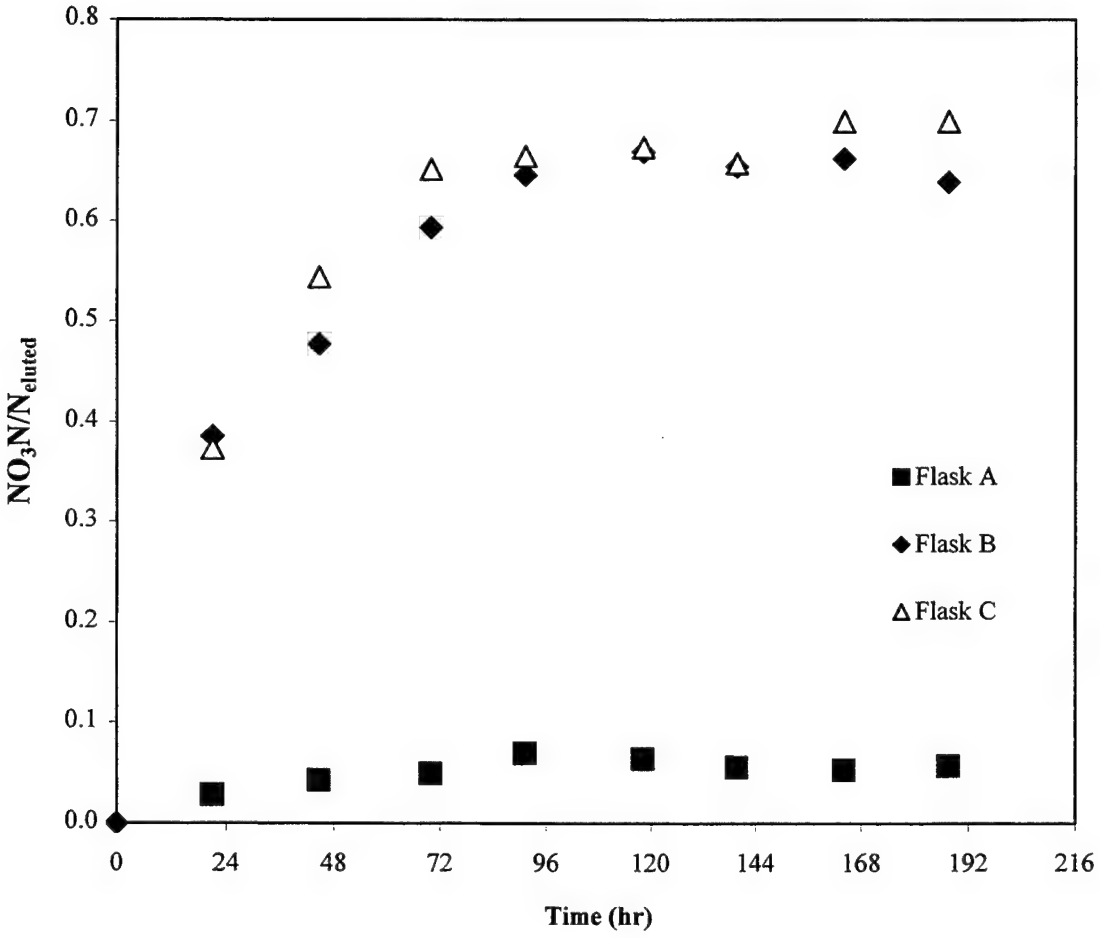

Figure 4.27: Nitrification efficiency for batch draw and fill experiment #1.

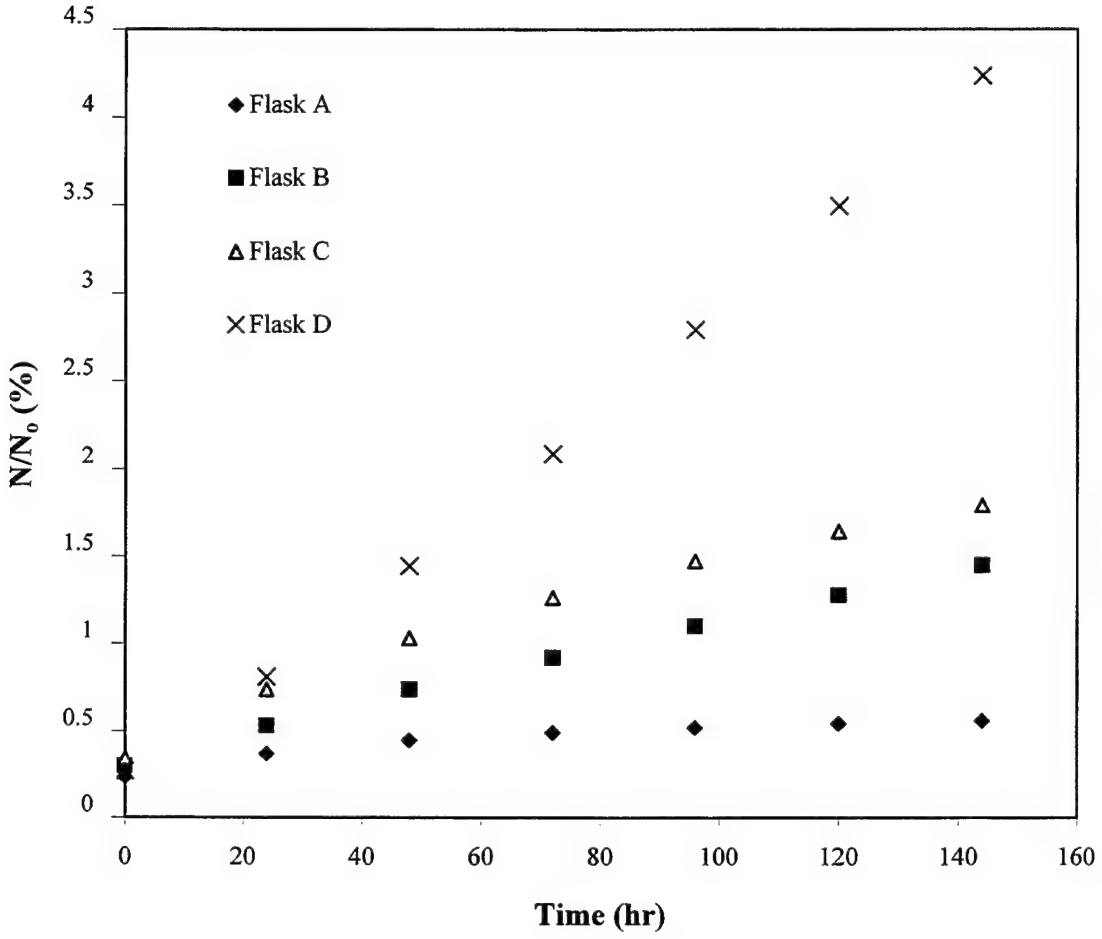

Figure 4.28: Regeneration efficiency for batch draw and fill experiment #2. Regeneration temperature = 22°C. Flask A and B contained no nitrifiers. Flask C and D were seed with 25 mL of washed nitrifiers. Deionized water was used as a regenerant for flasks A and C, while tap water was used as a regenerant for flasks B and D.

than it was in flask A. Additionally, the regeneration rate in flask C was 130 % higher than that of flask B, while the regeneration rate in flask D was 350 % higher than flask B.

Ammonia comprised 98 ± 1% and 99 ± 1% of the effluent nitrogen in flasks A and B. While the fraction ammonia in the effluent decreased in a manner similar to the first experiment. The range was 89 - 13% and 86 - 17% for flasks C and D respectively. Nitrification efficiency stabilized at 80% in flask D (Figure 4.29). Nitrification efficiency stabilized temporarily at 80% in flask C but continued to increase as the total available ammonia in the flask decreased.

Theoretically, there should not have been any ammonia in Flask A because there were no exchange ions present in the regenerant. The ammonia is believed to be from the adsorption phase. Even though the clinoptilolite was triple rinsed with deionized water after adsorption, all of the excess ammonia was probably not washed away. The manner in which the ammonia concentration decreases as the regenerant is applied looks similar to a dilution curve (Figure 4.30).

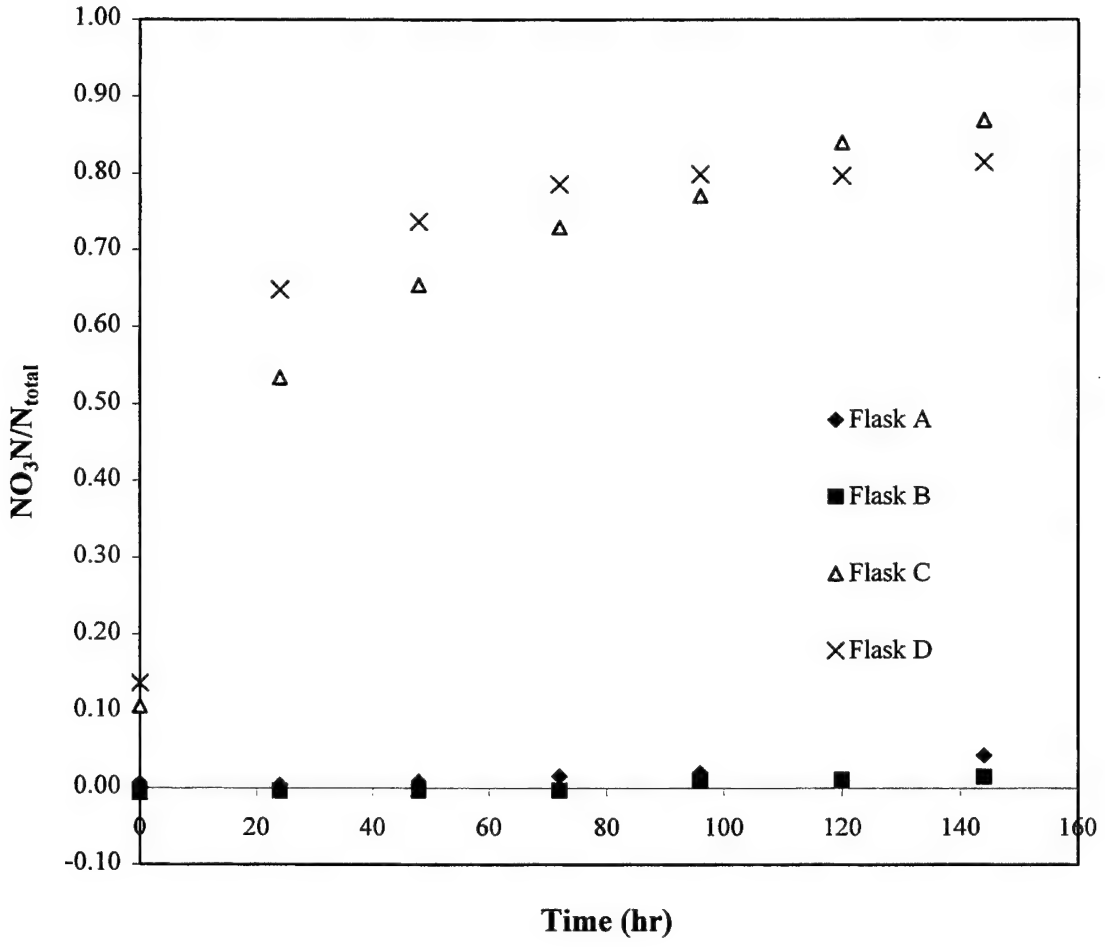

Figure 4.29: Nitrification efficiency for batch draw and fill experiment #2.

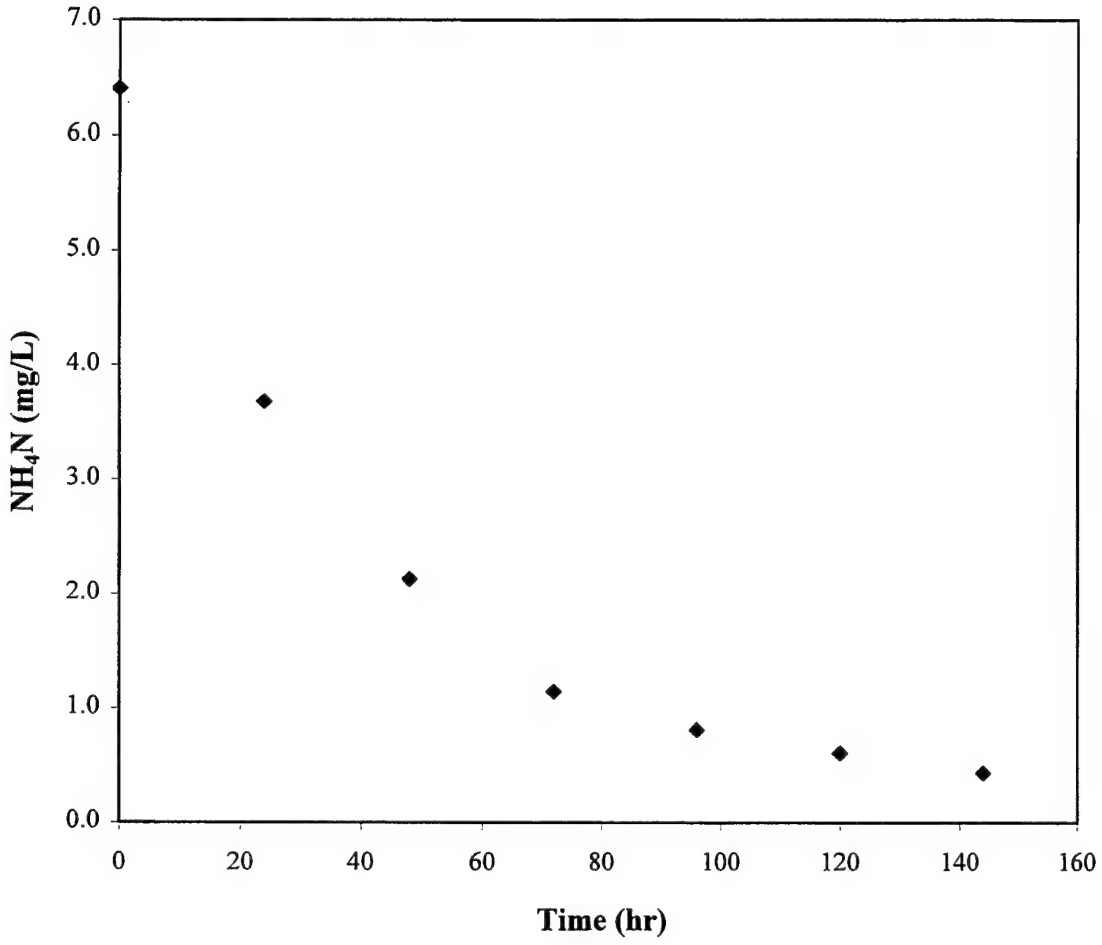

Figure 4.30: Supernatant ammonium concentration from flask A of batch draw and fill experiment #2.

CHAPTER 5
FULL-SCALE APPLICATION IN CONSTRUCTED WETLANDS

Clinoptilolite ion-exchange and in-situ bioregeneration technology is a feasible process that can be used to enhance nitrification in constructed wetland systems. Clinoptilolite beds can be used to retrofit existing CW systems, or to design and construct new systems. The beds are used to store ammonium during the winter months when conditions are not conducive for nitrification; they are then biologically regenerated during the warmer summer months when conditions are more conducive for nitrification.

5.1 Design

5.1.1 Physical Layout

The physical layout of a clinoptilolite bed CW system is shown Figure 6.1 and Figure 6.2. A sump and the clinoptilolite beds are the only additions to the CW system. Disinfection, if required, can be added to the process before discharging the effluent.

5.1.2 Sump

Effluent from the CW is used to regenerate the clinoptilolite bed. The purpose of the sump is to store enough effluent from the CW, so that it can be pumped quickly into the beds during the bioregeneration phase. If necessary ground water or water upstream from the discharge point can be used to supplement the wetland effluent. The effluent is pumped from the sump to the clinoptilolite bed; the pump should be sized to fill the bed in approximately one hour. The pump should be located externally from the sump to simplify maintenance access. The tanks should be covered to preclude algal

growth which might clog the clinoptilolite beds. The clinoptilolite beds may have fewer problems with suspended solids if they are proceeded by a SSF wetland.

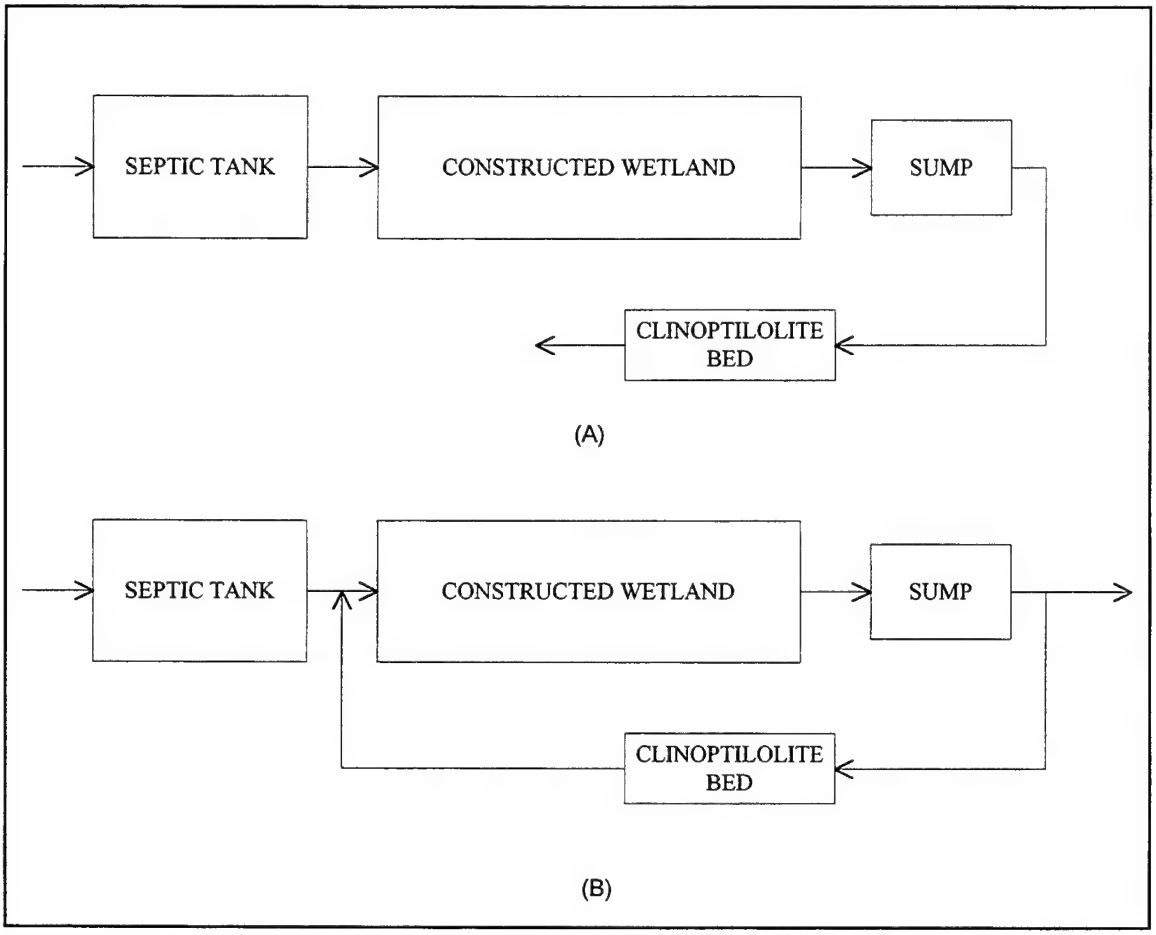

Figure 5.1: Wetland process diagram integrating clinoptilolite beds for enhanced nitrification. (A) Winter adsorption phase. (B) Summer bioregeneration phase.

5.1.3 Clinoptilolite Beds

Beds should be used for a CW system because they are easier to construct and maintain than columns. The beds can be constructed using the same simple techniques as those used to build a CW. They should be constructed in pairs, but connected in series. This is necessary because of the hydraulic requirements for regeneration (see Appendix C). A compacted clay liner or plastic liner can be used to prevent infiltration and leakage from/to the ground water.

The clinoptilolite must be conditioned before being put into service. After the clinoptilolite is placed in the beds a 0.5 M NaCl solution can be used to condition the clinoptilolite. The clinoptilolite should be conditioned using a NaCl solution, but conditioning has to be as minimal as possible, otherwise the cost of the exchanger will not be competitive compared to other materials (Haralambous *et al.*, 1992). Four fill and draw cycles with a three day detention time should suffice for this requirement. The clinoptilolite should be rinsed with several volumes of "clean" water to remove any excess sodium that may interfere with ammonium adsorption. However, there may be difficulty getting rid of the waste brine if the bed is conditioned in-situ. An alternative is to slurry the raw clinoptilolite with the NaCl mixture in a cement mixer before placing the clinoptilolite in the beds. The waste solution can be transported to a POTW for disposal. After rinsing the clinoptilolite, the trucks can be used to mix the nitrifiers with the clinoptilolite. A seed of nitrifiers can be obtained from any wastewater treatment plant with a nitrifying activated sludge. The bed is then ready to be put into service.

During the winter months, when nitrification is limited, the effluent from the CW is routed through the clinoptilolite beds. The ammonia/ammonium will be removed by the clinoptilolite and an ammonia free effluent is then discharged directly to the receiving water. Effluent concentrations of less than 2 mg/L can be expected and should be used as the breakthrough point for system operation.

During bioregeneration the effluent from the tank is used to fill the clinoptilolite beds in about an hour. The bed is allowed to remain saturated for about an hour before it is drained, and it remains drained until the next fill cycle. The beds should be regenerated at a rate of three fill and draw cycles every 2 days. The rate is limited by the availability of regenerant. Approximately one-half of the daily inflow is required for each regeneration cycle. It will take 75 days to regenerate each bed (150 days total) assuming 90% regeneration at 1.5 cyc/d, and 33% porosity. The time for regeneration will decrease as the porosity and fill cycles increase, and vice versa.

The nitrate-rich effluent is recirculated back to the head of the CW. The nitrate can be used as an alternate electron acceptor to reduce the BOD load from the

septic tank or lagoon. As an added benefit, the nitrate is converted to nitrogen gas via denitrification. Approximately 110 mg/L of BOD can be oxidized based on the maximum nitrate levels in the effluent. Theoretically, almost all of the ammonia captured during the six month adsorption phase can be completely removed from the CW as nitrogen gas. Therefore, the clinoptilolite process will remove approximately 50% of the annual ammonia load.

The beds should be designed with a high length-to-width ratio (L:W) for plug-flow. A minimum 10:1 (L:W) is recommended. The design adsorption capacity for the clinoptilolite is 1.9 mg NH_4N/g clinoptilolite based on an influent ammonia concentration of 25 mg NH_3N/L. These parameters are based upon experimental data using St. Cloud clinoptilolite. Clinoptilolite varies globally as well as locally. Therefore, if a different source of clinoptilolite is used a laboratory-scale adsorption experiment should be conducted to get a basic idea of the adsorption capacity. Note that static adsorption tests tend to over estimate the dynamic adsorption capacity (Cárázan *et al.*, 1988, Semmens *et al.*, 1978). There may be bioregeneration problems for CWs whose effluent has low alkalinity, low pH, or very high concentrations of potassium, calcium or magnesium.

5.2 Basic Cost Analysis

The additional costs associated with the clinoptilolite bed system include: capital costs for the pumping tank, pump, chemical conditioners, clinoptilolite, clinoptilolite bed, and plumbing to connect the system, and increased operational costs for pumping the regenerant. The clinoptilolite itself is fairly inexpensive. The St. Cloud Mining Company, located in New Mexico, charges $40 - $400 per ton depending on the particle size, packaging, quality and quantity control. However, the design can be optimized for nitrogen removal during the summer reducing the wetland area required to treat the incoming wastewater.

5.3 Operational Concerns

There are several operational concerns that must be addressed. First, will suspended solids (SS) loading from the constructed wetland effluent clog the clinoptilolite bed? Second, will the presence of nitrifying bacteria in the column cause fouling or cause a decrease in adsorption capacity? Third, will repeated adsorption and regeneration cycles decrease the adsorption capacity or cause a deterioration in column performance? The results of several other studies indicate that these concerns may not be significant.

In answer to the first question, Murphy *et al.* (1978) found little or no loss in capacity, and few operational problems for a clinoptilolite column loaded with a combined sewer overflow influent SS concentration of 20 - 50 mg/L (Linne and Semmens, 1985). The average SS concentration in CWs is often less this; Reed *et al.* (1995) reports that effluent SS concentrations in CWs are consistently less than 20 mg/L. A study conducted by Green et al. (1996) addresses the second consideration. They reported that there was no significant effect on the ion-exchange column efficiency with the presence of an attached biomass. Finally, Semmens *et al.* (1977b) reused a clinoptilolite column over 40 times without any significant fouling, loss of capacity, or deteriorated column performance.

CHAPTER 6
CONCLUSIONS

Based on the work and results of this study the following conclusions can be drawn:

1. Clinoptilolite can be used as an ion-exchange media to adsorb ammonium in temperatures as low as 4°C and the adsorption can be modeled using a Langmuir isotherm.

2. Ammonium-sorbed clinoptilolite can be bioregenerated using tap water, an in-situ nitrifying biomass, and either diffused aeration or draw and fill aeration. Either process can be used to remove almost 100% of the adsorbed ammonium. The nitrifying biomass can remove at least 94% of the ammonium as nitrate in ambient temperatures as low as 14°C when draw and fill regeneration is used. However, a clinoptilolite column can clog if an internal diffusor is used to supply air which will cause application problems.

3. Oxygen utilization is extremely efficient in the draw and fill bioregeneration scheme. The nitrifying biomass utilized from 68 - 95% of the available oxygen to oxidize the ammonium adsorbed by the clinoptilolite during the initial stages of regeneration.

4. The presence of a nitrifying biomass in an ammonium-sorbed clinoptilolite column increases the rate at which ammonium desorbs from the clinoptilolite. Ammonia oxidized to nitrate drives the desorption by causing a chemical gradient equilibrium shift in the desorption process. An in-situ nitrifying biomass can cut the regeneration time by at least one-half.

5. A clinoptilolite bed system will reduce CW design requirements. The design can be optimized for year-round BOD removal and summer-time nitrogen removal which will reduce the CW size under normal municipal waste conditions. Theoretically, a clinoptilolite bed system coupled with a CW system can be used to remove almost 100% of the wetland's effluent ammonia during the six month adsorption phase. After the ammonia is converted to nitrate the nitrate can be used to decrease the influent BOD concentration into the CW.

Overall, this study shows that it is feasible to use a clinoptilolite based system to adsorb ammonium in temperatures typically found during the winter months and biologically regenerate the ammonium-sorbed clinoptilolite using a low-strength cation regenerant with an in-situ nitrifying biomass and utilizing passive aeration.

CHAPTER 7
FUTURE WORK

This study provides insight into the feasibility and applicability of using ion exchange and passive aeration for enhancing nitrification in constructed wetland systems. However, there are many potential research avenues that need to be explored.

① The system limitations need to be defined. Additional laboratory-scale studies should be conducted to determine:

- The minimum cation concentration necessary to regenerate ammonium-sorbed clinoptilolite within the six month regeneration parameter.
- The minimum alkalinity requirements to prevent nitrifier and subsequently regeneration inhibition.
- The minimum temperature required for bioregeneration.

② A field-scale study is needed to demonstrate the concept and design, and gather important information on the system's operating parameters. The ideal scenario for this study would be to use an existing constructed wetland, with nitrogen removal problems, in a mid- to northern-tier location, that has a well established database of influent and effluent parameters.

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APPENDICES

APPENDIX A. St. Cloud Clinoptilolite Physical Properties

APPENDIX A

ST. CLOUD CLINOPTILOLITE PHYSICAL PROPERTIES

Property	**Value**
Acid stability (pH)	0 - 7
Alkali stability (pH)	7 - 13
Bulk density - solid, dried (lb/ft^3)	87
(kg/m^3)	1390
Bulk density - aggregate, dried (lb/ft^3)	
4 x 6 mesh	44 - 48
6 x 14 mesh	45 - 47
14 x 40 mesh	46 - 49
- 40 mesh	48 - 52
Cation exchange capacity (meq/g)	1.0 - 2.2
Molecular ratio (Si:Al)	5:1
pH	8.0 (approx.)
Pore size (Å)	4.0
Pore volume (%)	52
Specific gravity	2.2 - 2.4
Surface area (yd^2/oz)	1357
(m^2/g)	40

Nominal Particle Size	Percent Retained (14 - 40 mesh)
1 inch - 8 mesh	0.00
14 mesh	0.12
20 mesh	41.98
40 mesh	53.66
70 mesh	n/a
100 mesh	4.62
<100 mesh	0.61
Typical moisture content (%)	3.8
Typical density (lbs/ft^3)	49.0

APPENDIX B. Raw Data

APPENDIX B - RAW DATA

B.1 Adsorption Study

B.1.1 Unconditioned Clinoptilolite

Feed Solution	NH_4N_{avg} (mg/L)
A	48.67267
B	95.58001
C	95.8322

Sample Number	Mass (g)	Feed Solution	T (oC)	pH	Cw (mg NH4N/L)	Cs (mg/g)
1	1.7175	B	22.5	6.88	65.49	1.73
2	4.5432	C	22.5	7.13	41.86	1.18
3	0.7302	A	22.5	6.34	35.39	1.82
4	1.825	A	22.7	6.56	25.89	1.25
5	4.6763	A	22.5	6.88	14.67	0.73
6	7.1382	A	22.5	7.01	10.48	0.54
7	7.9339	A	22.5	7.05	9.52	0.49
8	10.1889	A	22.4	7.07	7.65	0.40
9	14.7642	A	22.6	7.18	7.17	0.28
10	19.3999	A	22.6	7.24	5.26	0.22

B.1.2 NaCl-(NH4)2SO4-NaCl Conditioned Clinoptilolite

Feed Solution	NH_4N_{avg} (mg/L)
A	95.3
B	182.1
C	47.7

Sample Number	Mass (g)	Feed Solution	T (^oC)	pH	C_w (mg NH_4N/L)	C_s (mg/g)
1	1.2402	B	20.4	6.38	128.6	4.31
2	1.5015	A	20.2	6.65	40.2	3.67
3	3.3817	A	20.3	6.87	16.2	2.33
4	0.9884	C	20.4	6.72	15.9	3.21
6	6.6051	C	20.4	7.3	2.5	0.68
7	10.6742	C	20.3	7.37	2.0	0.43
8	14.4729	C	20.3	7.42	1.9	0.32
9	20.7636	C	20.4	7.49	1.7	0.22
10	30.1998	C	20.2	7.58	1.7	0.15

B.1.3 NaCl Conditioned Clinoptilolite

Feed Solution	NH_4N_{avg} (mg/L)
A	189.2
B	97.0
C	49.2

Sample Number	Mass (g)	Feed Solution	T (°C)	pH	C_w (mg NH_4N/L)	C_s (mg/g)
1	0.6579	A	21.6	6.02	160.7	4.33
2	1.1818	B	21.7	5.91	53.7	3.66
3	1.2822	C	21.8	6.37	17.7	7.34
4	2.7966	C	21.8	6.74	7.2	3.74
5	5.082	C	21.8	6.97	3.8	2.12
6	7.9268	C	21.7	7.12	2.9	1.37
7	11.7369	C	21.8	7.23	2.4	0.93
8	18.6642	C	21.9	7.27	3.7	0.58
9	28.1412	C	21.9	7.37	2.6	0.39
10	37.0104	C	22.0	7.38	1.8	0.30

B.2 NaCl Conditioning Study

Sample Number	T (°C)	NaCl (mol/L)	C_w (mg NH_4N/L)	C_s (mg/g)
Blank	22.3	0.00	8.72	0.26
A	21.9	0.17	2.69	0.29
B	22	0.33	1.97	0.29
C	21.8	0.50	1.71	0.29
D	22	0.57	1.69	0.29
E	22	0.84	1.59	0.29
F	22	1.00	1.59	0.29

B.3 Biological Regeneration Batch Feasibility Study

B.3.1 First Series

B.3.1.1 Reactor A

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
0:00	22.4	8.78				
1:00	23.5	8.74	0.9	0.00	2.2	0.11
3:30	24.5	8.66	1.4	0.00		
7:00	25.5	8.55	2.2	0.00		
11:20	25.0	8.4	3.1	0.00		
21:20	23.8	8.39	5.6	0.01	4.1	0.18
47:25	20.6	8.34	10.5	0.03	7.0	0.27
70:55	21.6	8.33	14.9	0.00	4.5	0.08
94:10	21.8	8.45	17.7	0.09	0.6	0.21
116:55	21.9	8.44	19.6	0.04	0.3	0.03
154:30	22.8	8.46	22.2	0.03		
188:45	22.3	8.51	23.7	0.03		
237:00	22.4	8.58	24.4	0.09		
333:10	22.8	8.6	26.5	0.24		

B.3.1.2 Reactor B

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
0:00	22.4	8.78				
1:00	23.4	8.74	0.8	0.01	1.6	
3:30	24.4	8.68	1.3	0.00		
7:00	25.5	8.57	2.1	0.00		
11:20	24.9	8.43	3.1	0.01		
21:20	23.8	8.41	5.7	0.00	3.7	0.17
47:25	20.5	8.39	11.2	0.01	2.8	0.06
70:55	21.5	8.35	15.0	0.07	5.6	0.15
94:10	21.6	8.47	17.8	0.14	0.6	0.12
116:55	21.8	8.45	19.3	0.03	0.9	0.08
154:30	22.8	8.48	22.0	0.02		
188:45	22.3	8.54	23.0	0.04		
237:00	22.4	8.62	24.2	0.05		
333:10	22.7	8.68	26.7	0.00		

B.3.1.3 Reactor C

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
0:00	22.5	8.78				
1:00	23.5	8.71	0.8	0.01	3.4	0.06
3:30	24.5	8.68	1.3	0.00		
7:00	25.5	8.57	2.0	0.00		
11:20	25.0	8.44	3.0	0.00		
21:20	23.9	8.43	5.3	0.01	4.2	0.09
47:25	20.6	8.44	9.7	0.02	4.8	0.09
70:55	21.6	8.35	13.6	0.02	5.5	0.13
94:10	21.7	8.44	17.1	0.00	0.7	0.08
116:55	21.8	8.41	19.1	0.03	0.3	0.08
154:30	22.9	8.45	22.6	0.03		
188:45	22.3	8.49	23.8	0.00		
237:00	22.4	8.61	25.0	0.00		
333:10	22.7	8.67	27.7	0.09		

B.3.1.4 Control

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
0:00	22.4	8.55			34.3	2.04
1:00	23.6	8.52	0.7	0.01	32.1	0.62
3:30	24.6	8.47	1.1	0.00		
7:00	25.5	8.40	1.5	0.00		
11:20	25.0	8.32	2.0	0.01		
21:20	23.8	8.35	3.4	0.01	16.3	0.00
47:25	20.7	8.28	7.1	0.00	12.4	0.16
70:55	21.8	8.11	13.0	0.01	6.4	0.06
94:10	21.8	8.46	16.9	0.03	0.4	0.08
116:55	22.0	8.50	17.2	0.00	0.2	0.08
154:30	23.0	8.52	17.7	0.02		
188:45	22.5	8.55	18.2	0.07		

B.3.2 Second Series

B.3.2.1 Reactor A

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
1:02	21.8	8.57	0.9	0.01	3.1	0.01
3:30	21.5	8.55	1.4	0.02	4.0	0.13
6:44	21.7	8.54	2.2	0.02	3.5	0.03
12:02	22.1	8.39	3.8	0.04	2.9	0.05
23:48	21.4	8.35	7.6	0.02	1.6	0.01
46:41	22.3	7.95	16.2	0.09	0.5	0.00
69:20	20.7	8.05	19.3	0.05	0.3	0.00
117:05	21.0	8.43	23.3	0.14	0.4	0.01
166:45	21.6	8.29	25.7	0.00	0.2	0.01
239:41	21.5	8.25	28.9	0.05	0.2	0.01
313:24	21.5	8.13	30.5	0.64	0.2	0.01

B.3.2.2 Reactor B

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
1:02	21.8	8.64	0.9	0.01	3.2	0.01
3:31	21.5	8.61	1.4	0.00	4.0	0.24
6:46	21.8	8.56	2.2	0.01	3.5	0.02
12:06	21.9	8.42	4.2	0.21	2.7	0.03
23:50	20.9	8.29	8.0	0.00	1.4	0.01
46:43	22.3	8.07	15.8	0.05	0.6	0.00
69:21	20.8	8.08	19.2	0.63	0.3	0.01
117:07	21.1	8.43	22.9	0.00	0.3	0.00
166:47	21.7	8.33	25.9	0.05	0.2	0.01
239:43	21.6	8.3	28.7	0.05	0.2	0.01
313:26	21.5	8.19	29.6	0.40	0.2	0.00

B.3.2.3 Reactor C

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
1:03	21.8	8.64	0.9	0.01	3.2	0.01
3:33	21.5	8.62	1.4	0.00	3.9	0.14
6:48	21.8	8.55	2.3	0.01	3.6	0.03
12:09	22.0	8.51	3.9	0.00	2.9	0.02
23:52	21.1	8.36	7.4	0.08	1.9	0.01
46:45	22.3	8.11	14.4	0.08	0.9	0.01
69:23	20.8	8.03	19.3	0.18	0.3	0.01
117:09	21.1	8.43	23.6	0.00	0.3	0.01
166:49	21.8	8.31	26.7	0.05	0.2	0.01
239:45	21.7	8.28	29.7	0.00	0.2	0.01
313:27	21.5	8.15	31.4	0.00	0.2	0.01

B.3.2.4 Control

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
0:00	0.0	0.00			31.3	0.67
1:06	21.8	8.57	0.7	0.00	29.8	0.15
4:23	21.5	8.55	1.3	0.01	25.9	0.07
9:46	21.7	8.54	2.4	0.05	23.9	0.05
20:26	22.1	8.39	5.9	0.08	19.2	0.00
44:19	22.3	7.71	15.8	0.00	10.2	0.07
66:59	20.9	8.2	23.3	0.23	0.4	0.01
114:47	21.2	8.49	25.8	0.11	0.3	0.01
164:24	21.8	8.45	24.1	0.11	0.2	0.01

B.3.3 Third Series

B.3.3.1 Reactor A

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
0:00	21.8	8.67				
0:59	22.0	8.67	0.8	0.01	3.0	0.03
2:55	22.3	8.61	1.2	0.01	3.4	0.03
5:28	23.0	8.55	1.7	0.01	3.5	0.03
12:05	24.1	8.18	3.6	0.00	2.9	0.04
23:55	22.8	8.2	8.8	0.02	1.1	0.01
47:35	23.0	8.28	16.0	0.09	0.3	0.01
71:51	23.0	8.32	19.5	0.05	0.2	0.01
106:34	24.2	8.27	22.3	0.45	0.2	0.01
143:47	21.9	8.4	24.9	0.08	0.2	0.01
192:18	24.0	8.18	27.0	0.05	0.2	0.00
261:19	24.7	7.94	28.8	0.05	0.2	0.00
334:40	23.9	8.12	32.0	0.16	0.2	0.01

B.3.3.2 Reactor B

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
0:00	21.8	8.76				
0:59	21.8	8.66	0.8	0.01	2.9	0.03
2:54	22.1	8.61	1.1	0.00	3.2	0.03
5:27	22.8	8.56	1.6	0.00	3.4	0.02
12:05	23.9	8.2	3.5	0.08	2.9	0.03
23:55	22.5	8.28	7.7	0.09	1.5	0.02
47:34	22.8	8.31	13.4	0.02	0.6	0.01
71:49	22.8	8.33	17.1	0.05	0.5	0.01
106:33	23.9	8.3	20.8	0.05	0.2	0.01
143:46	21.7	8.42	24.0	0.54	0.3	0.01
192:17	23.7	8.22	26.5	0.08	0.2	0.01
261:18	24.3	7.98	28.2	0.08	0.3	0.01
334:39	23.7	8.17	31.1	0.08	0.3	0.01

B.3.3.3 Reactor C

Time (hr:min)	T °C	pH	NO_3N (mg/L)	STD DEV	NH_4N (mg/L)	STD DEV
0:00	21.8	8.77				
0:57	21.9	8.67	0.8	0.00	3.0	0.02
2:53	22.2	8.63	1.1	0.00	3.4	0.03
5:26	22.8	8.57	1.6	0.00	3.5	0.01
12:03	24.0	8.28	3.4	0.01	2.9	0.05
23:53	22.7	8.35	7.1	0.04	1.7	0.02
47:33	23.0	8.32	13.3	0.04	0.6	0.01
71:48	22.8	8.33	17.1	2.22	0.4	0.01
106:31	24.0	8.32	21.2	0.05	0.2	0.00
143:44	21.8	8.42	24.1	0.05	0.3	0.00
192:15	23.8	8.22	27.4	0.00	0.2	0.00
261:16	24.4	7.98	29.2	0.05	0.2	0.01
334:38	23.6	8.12	32.0	0.18	0.3	0.01

B.4 Column Studies

B.4.1 Prototype

Sample #	Cum. Time (hr:min)	BV	DO (mg/L)	pH	NO_3N (mg/L)	NO_3N (mg)	NH_3N (mg/L)	NH_3N (mg)	NH_4N_{eluted} (mg/L)	$N_{removed}$ (%)	$Alk_{consumed}$ (mg/L as $CaCO_3$)
1	0:00	0.00			0.6	0.5	3.1	2.6	3.7	0.1	
2	7:40	1.08	2.30	7.88	2.2	6.2	5.3	14.9	7.6	0.6	
3	19:40	2.77	1.75	8.06	4.0	17.6	9.7	42.3	13.7	1.9	
4	31:40	4.46	2.15	7.95	4.4	19.1	10.4	45.4	14.8	3.4	
5	43:40	6.15	3.00	7.99	6.7	29.2	6.5	28.4	13.2	4.8	
6	55:40	7.85	2.15	7.93	9.0	39.3	6.0	26.2	15.0	6.3	
7	67:40	9.54	2.24	7.94	10.0	43.5	6.5	28.3	16.5	7.9	67.9
8	91:40	12.92	2.26	7.87	15.0	130.9	6.6	58.0	21.6	12.3	87.3
9	115:40	16.30	2.07	7.78	24.0	209.9	4.8	42.0	28.9	18.1	135.7
10	139:40	19.68	2.30	7.54	31.2	272.2	6.1	53.6	37.3	25.7	194.2
11	163:40	23.07	2.40	7.28	35.9	313.4	4.5	38.9	40.4	33.8	236.0
12	187:40	26.45	N/A	7.41	35.7	363.1	1.3	13.7	37.1	42.6	N/A
13	211:40	29.83	5.31	7.38	31.8	277.4	1.0	8.4	32.7	49.2	205.9
14	235:40	33.21	1.95	6.96	35.6	310.5	0.7	6.2	36.3	56.5	234.9
15	259:40	36.59	2.32	7.1	34.8	303.7	0.7	5.9	35.5	63.7	230.1
16	283:21	39.93	2.44	7.37	28.4	244.6	0.7	5.7	29.1	69.5	197.4
17	307:40	43.36	2.95	7.57	27.7	244.5	0.3	2.8	28.0	75.2	194.7
18	331:40	46.74	2.70	7.78	22.6	197.0	0.2	1.6	22.8	79.8	152.3
19	355:40	50.12	2.66	7.67	18.3	159.7	0.2	1.8	18.5	83.5	134.2
20	379:40	53.51	2.94	7.88	16.4	143.1	0.1	0.7	16.5	86.8	117.6
21	403:40	56.89	3.55	8.00	14.5	127.0	0.1	0.8	14.6	89.8	102.4
22	427:40	60.27	4.84	8.04	12.8	111.9	0.1	1.0	12.9	92.4	88.8
23	451:00	63.56	3.50	7.93	10.7	91.1	0.2	1.8	10.9	94.6	75.2
24	475:40	67.04	4.95	8.03	9.9	88.9	0.1	0.9	10.0	96.6	69.2
25	499:40	70.42	5.22	7.97	9.0	78.5	0.1	0.6	9.1	98.5	65.1
26	523:40	73.80	5.10	8.20	7.8	68.3	0.1	0.5	7.9	100.1	57.1
27	547:40	77.18	5.57	8.27	6.8	58.9	0.1	1.3	6.9	101.5	38.9
28	571:40	80.57	6.30	8.33	5.6	49.1	0.0	0.4	5.7	102.6	36.9
29	595:40	83.95	6.10	8.26	4.9	42.6	0.1	0.6	4.9	103.6	57.5
30	617:55	87.08	6.20	8.28	4.1	32.8	0.1	0.7	4.2	104.4	52.0
31	643:40	90.71	6.39	8.45	3.6	33.3	0.1	1.0	3.7	105.2	48.0
32	666:10	93.88	6.78	8.53	3.2	26.0	0.1	0.4	3.2	105.8	44.0

B.4.2 Adsorption

B.4.2.1 Feed

Sample Number	Date/Time	T_{feed} (°C)	NH_3N_{AVG} (mg/L)	STD DEV	Vol_{used} (L)
0	10/6/98 7:30	2.0	26.8	0.06	
1	10/6/98 11:05	2.0	26.6	0.22	
2	10/6/98 15:00	2.0	26.5	0.10	
3	10/6/98 19:10	2.0	25.7	0.06	99
4	10/6/98 23:30	2.0	26.3	0.06	
5	10/7/98 5:37	8.0	26.2	0.06	89
6	10/7/98 8:55	5.5	25.8	0.06	
7	10/7/98 13:00	5.0	26.3	0.06	
8	10/7/98 16:58	6.0	25.7	0.10	95
9	10/7/98 22:00	4.5	25.8	0.00	
10	10/8/98 3:55	6.0	26.2	0.10	95
11	10/8/98 10:30	4.0	25.9	0.06	
12	10/8/98 16:00	5.5	25.2	0.10	110
13	10/8/98 21:45	5.5	25.3	0.06	
14	10/9/98 4:02	5.5	26.9	0.06	100

B.4.2.2 Column A

Sample Number	Date/Time	T_{feed} (°C)	NH_3N_{AVG} (mg/L)	STD DEV
0	10/6/98 7:30	2.0	0.3	0.01
1	10/6/98 11:05	2.0	0.2	0.01
2	10/6/98 15:00	2.0	0.2	0.01
3	10/6/98 19:10	2.0	0.2	0.05
4	10/6/98 23:30	2.0	0.1	0.01
5	10/7/98 5:37	8.0	0.3	0.01
6	10/7/98 8:55	5.5	2.8	0.01
6.5	10/7/98 11:37	5.0	7.0	0.03
7	10/7/98 13:00	5.0	8.6	0.00
7.5	10/7/98 14:55		11.7	0.03
8	10/7/98 16:58	6.0	15.1	0.12
9	10/7/98 22:00	4.5	19.6	0.12
10	10/8/98 3:55	6.0	21.3	0.06
10.5	10/8/98 6:16	6.0	22.0	0.12
11	10/8/98 10:30	4.0	22.7	0.12
12	10/8/98 16:00	5.5	22.7	0.06
13	10/8/98 21:45	5.5	23.0	0.10
14	10/9/98 4:02	5.5	23.5	0.10

B.4.2.3 Column B

Sample Number	Date/Time	T_{feed} (°C)	NH_3N_{AVG} (mg/L)	STD DEV
0	10/6/98 7:30	2.0	0.2	0.01
1	10/6/98 11:05	2.0	0.1	0.00
2	10/6/98 15:00	2.0	0.2	0.00
3	10/6/98 19:10	2.0	0.1	0.01
4	10/6/98 23:30	2.0	0.2	0.01
5	10/7/98 5:37	8.0	0.2	0.00
6	10/7/98 8:55	5.5	0.1	0.00
7	10/7/98 13:00	5.0	0.1	0.01
8	10/7/98 16:58	6.0	0.3	0.00
9	10/7/98 22:00	4.5	0.2	0.00
10	10/8/98 3:55	6.0	0.1	0.00
11	10/8/98 10:30	4.0	0.2	0.01
12	10/8/98 16:00	5.5	1.3	0.01
12.5	10/8/98 18:15	5.5	3.4	0.00
13	10/8/98 21:45	5.5	8.1	0.08
14	10/9/98 4:02	5.5	15.4	0.12

B.4.2.4 Column C

Sample Number	Date/Time	T_{feed} (°C)	NH_3N_{AVG} (mg/L)	STD DEV
0	10/6/98 7:30	2.0	0.3	0.01
2	10/6/98 15:00	2.0	0.1	0.00
3	10/6/98 19:10	2.0	0.1	0.00
4	10/6/98 23:30	2.0	0.1	0.00
5	10/7/98 5:37	8.0	0.1	0.01
6	10/7/98 8:55	5.5	0.1	0.00
7	10/7/98 13:00	5.0	0.2	0.00
9	10/7/98 22:00	4.5	0.2	0.00
10	10/8/98 3:55	6.0	0.2	0.00
11	10/8/98 10:30	4.0	0.2	0.00
12	10/8/98 16:00	5.5	0.2	0.00
13	10/8/98 21:45	4.5	0.1	0.01
14	10/9/98 4:02	6.0	0.1	0.01

B.4.3 Regeneration

B.4.3.1 Column A

Sample	Time (hr:min)	BV	NO_3N (mg/L)	STD DEV	NH_3N (mg/L)	STD DEV	$Alk_{consumed}$ (mg/L as $CaCO_3$)
0	0:00	0.00	2.1	0.01	18.7	0.16	
1	23:46	5.25	1.1	0.01	18.0	0.10	
2	44:50	9.91	0.8	0.02	16.1	0.06	5.0
3	57:50	12.78	0.9	0.01	14.7	0.06	2.0
4	72:10	15.95	0.9	0.00	13.6	0.10	3.0
5	77:40	17.16	0.9	0.00	12.9	0.11	0.0
6	93:55	20.75	1.6	0.02	11.8	0.03	12.0
7	118:45	26.24	1.6	0.01	11.6	0.03	10.0
8	141:40	31.30	1.9	0.00	11.0	0.05	10.0
9	166:40	36.83	1.9	0.00	10.3	0.05	8.0
10	190:40	42.13	2.0	0.01	9.8	0.05	11.0
11	212:15	46.90	2.0	0.02	9.4	0.02	17.0
12	239:00	52.81	2.2	0.01	9.1	0.09	
13	262:00	57.89	2.3	0.00	8.3	0.02	14.0
14	287:00	63.42	2.6	0.13	8.3	0.02	
15	291:30	64.41	2.8	0.05	8.0	0.02	
16	310:00	68.50	3.3	0.03	7.6	0.03	32.9
17	335:20	74.10	3.3	0.00	7.4	0.04	40.0
18	356:30	78.77	3.8	0.09	6.9	0.06	57.0
19	380:27	84.07	4.6	0.05	6.6	0.03	71.3
20	407:07	89.96	5.3	0.21	5.9	0.04	85.0
21	429:40	94.94	6.6	0.10	5.4	0.03	
22	455:37	100.67	7.6	0.20	4.7	0.02	121.3
23	477:40	105.55	22.3	0.02	4.8	0.03	
24	502:35	111.05	14.4	0.02	4.3	0.01	
25	524:10	115.82	13.0	0.06	3.9	0.01	
26	548:30	121.20	14.9	0.02	3.6	0.02	
27	575:05	127.07	19.8	0.00	3.2	0.01	
28	597:40	132.06	23.5	0.05	3.0	0.01	
29	621:55	137.42	27.4	0.00	2.8	0.03	
30	646:40	142.89	29.1	0.08	2.5	0.01	
31	670:20	148.12	33.7	0.05	2.4	0.01	
32	694:40	153.50	37.8	0.08	2.3	0.01	
33	716:40	158.36	18.8	0.05	1.8	0.01	
34	743:40	164.32	23.0	0.05	1.8	0.01	
35	766:15	169.31	30.8	0.12	1.8	0.01	
36	791:20	174.86	18.1	0.14	1.6	0.01	
37	814:10	179.90	13.8	0.04	1.5	0.01	
38	839:20	185.46	13.3	0.02	1.5	0.01	
39	861:10	190.29	13.6	0.01	1.2	0.01	
40	863:15	190.75	12.4	0.02	0.9	0.01	
41	884:45	195.50	26.6	0.25	0.5	0.01	
42	910:40	201.22	24.1	0.18	0.5	0.01	
43	933:40	206.31	22.9	0.05	0.5	0.01	

B.4.3.2 Column B

Sample	Time (hr:min)	BV	NO_3N (mg/L)	STD DEV	NH_3N (mg/L)	STD DEV	$Alk_{consumed}$ (mg/L as $CaCO_3$)
0	0:00	0.00	41.8	0.05	11.7	0.08	
1	21:55	4.99	3.0	0.03	10.3	0.06	
2	43:30	9.91	1.5	0.01	9.9	0.06	14.0
3	70:15	16.00	1.3	0.02	9.3	0.04	
4	93:15	21.24	1.2	0.00	8.6	0.04	17.0
5	118:15	26.94	1.1	0.03	8.1	0.02	
6	141:20	32.20	1.4	0.02	7.0	0.04	10.0
7	166:40	37.97	1.9	0.02	7.0	0.01	
8	170:45	38.90	1.8	0.02	4.7	0.04	
9	170:45	38.90	1.2	0.02	2.9	0.04	
10	187:50	42.79	2.5	0.02	6.0	0.05	
11	211:45	48.24	2.6	0.03	5.7	0.04	
12	238:25	54.32	3.3	0.02	4.9	0.04	
13	260:55	59.44	3.1	0.01	4.9	0.03	
14	286:55	65.37	3.8	0.10	4.5	0.02	
15	308:55	70.38	4.8	0.02	4.2	0.02	
16	333:55	76.07	7.4	0.03	3.7	0.02	
17	355:25	80.97	12.8	0.00	2.8	0.02	
18	379:45	86.51	18.9	0.05	2.4	0.02	
19	406:20	92.57	21.7	0.02	2.1	0.01	
20	428:55	97.72	24.7	0.00	2.0	0.01	
21	453:10	103.24	24.1	0.12	1.6	0.01	
22	477:40	108.82	25.4	0.09	1.4	0.01	
23	501:35	114.27	26.5	0.20	1.5	0.01	
24	525:55	119.81	47.2	0.05	1.3	0.01	
25	547:55	124.83	30.5	0.08	1.5	0.03	
26	575:05	131.02	19.6	0.12	1.7	0.02	
27	597:30	136.12	10.0	0.05	1.4	0.02	
28	622:30	141.82	10.7	0.02	1.1	0.02	
29	645:21	147.02	9.7	0.02	1.1	0.01	

B.4.3.3 Column C

Sample	Time (hr:min)	BV	NO_3N (mg/L)	STD DEV	NH_3N (mg/L)	STD DEV
0	0:00	0.0	5.0	0.03	1.2	0.01
1	3:25	0.6	1.9	0.01	0.6	0.00
2	23:46	4.1	1.5	0.00	0.3	0.01
3	44:50	7.8	2.3	0.02	0.3	0.04
4	57:50	10.0	2.5	0.04	0.2	0.00
5	72:10	12.5	2.1	0.02	0.3	0.00
6	77:40	13.5	2.2	0.01	0.3	0.00
7	94:10	16.3	2.2	0.03	0.3	0.00
8	118:45	20.6	2.6	0.04	0.3	0.00
9	141:40	24.6	3.0	0.01	0.2	0.00
10	166:40	28.9	3.5	0.02	0.2	0.00
11	190:40	33.1	4.2	0.01	0.1	0.00
12	212:15	36.8	4.7	0.03	0.1	0.00
13	239:00	41.5	4.8	0.03	0.1	0.00
14	262:00	45.5	5.1	0.03	0.1	0.00
15	287:00	49.8	5.5	0.06	0.1	0.00
16	310:00	53.8	5.8	0.12	0.1	0.00
17	335:20	58.2	6.2	0.03	0.1	0.00
18	356:30	61.8	6.7	0.04	0.1	0.01
19	380:27	66.0	7.9	0.06	0.1	0.01
20	407:07	70.6	7.8	0.07	0.1	0.00
21	429:40	74.5	7.0	0.12	0.1	0.00
22	455:38	79.0	5.8	0.03	0.1	0.00
23	477:40	82.9	5.3	0.02	0.1	0.00
24	502:35	87.2	4.7	0.02	0.1	0.00
25	524:10	90.9	4.0	0.00	0.3	0.00
26	548:30	95.2	3.6	0.00	0.1	0.01
27	575:05	99.8	3.2	0.00	0.1	0.01
28	597:40	103.7	2.9	0.00	0.1	0.00
29	621:55	107.9	2.3	0.02	0.1	0.00
30	646:40	112.2	1.9	0.00	0.1	0.00
31	670:20	116.3	2.0	0.01	0.1	0.00
32	694:40	120.5	1.5	0.00	0.1	0.00

B.5 Draw and Fill with Passive Aeration

B.5.1 Batch Studies

B.5.1.1 Experiment #1

B.5.1.1.1 Flask A

Time (hr:min)	NO_3N_{avg} (mg/L)	STD DEV	NH_4N_{avg} (mg/L)	STD DEV
0:00	0.0	0.00	0.0	0.00
21:00	0.3	0.00	9.3	0.03
44:40	0.3	0.00	7.4	0.05
69:55	0.3	0.00	6.6	0.00
91:20	0.4	0.02	5.1	0.04
118:15	0.4	0.01	5.1	0.01
139:40	0.4	0.00	6.4	0.02
164:05	0.4	0.01	6.4	0.04
187:35	0.4	0.01	6.0	0.04

B.5.1.1.2 Flask B

Time (hr:min)	NO_3N_{avg} (mg/L)	STD DEV	NH_4N_{avg} (mg/L)	STD DEV
0:00	0.0	0.00	0.0	0.00
21:00	3.8	0.00	6.1	0.05
44:40	6.7	0.02	7.3	0.04
69:55	7.8	0.02	5.4	0.00
91:20	7.7	0.05	4.2	0.03
118:15	10.5	0.04	5.2	0.03
139:40	11.1	0.05	5.9	0.03
164:05	10.1	0.05	5.1	0.01
187:35	8.7	0.02	4.9	0.03

B.5.1.1.3 Flask C

Time (hr:min)	NO_3N_{avg} (mg/L)	STD DEV	NH_4N_{avg} (mg/L)	STD DEV
0:00	0.0	0.00	0.0	0.00
21:00	4.2	0.02	7.0	0.08
44:40	7.0	0.03	5.9	0.01
69:55	8.0	0.00	4.3	0.04
91:20	8.1	0.02	4.1	0.01
118:15	8.0	0.06	3.8	0.03
139:40	9.1	0.02	4.7	0.05
164:05	8.3	0.05	3.6	0.02
187:35	8.3	0.05	3.6	0.02

B.5.1.2 Experiment #2

Flask	Date	NH_4N (mg/L)	STD DEV	NO_2N (mg/L)	NO_3N (mg/L)
Feed 1	13-Apr	0.0	0.00	0.0	0.0
Feed 2	13-Apr	0.1	0.01	0.0	0.2
A	13-Apr	6.4	0.02	0.0	0.0
	14-Apr	3.7	0.03	0.0	0.0
	15-Apr	2.1	0.01	0.0	0.0
	16-Apr	1.1	0.02	0.0	0.0
	17-Apr	0.8	0.01	0.0	0.0
	18-Apr	0.6	0.02	0.0	0.0
	19-Apr	0.4	0.01	0.0	0.0
B	13-Apr	8.1	0.02	0.0	-0.1
	14-Apr	6.5	0.02	0.0	0.0
	15-Apr	5.7	0.02	0.0	0.0
	16-Apr	4.9	0.02	0.0	0.0
	17-Apr	4.9	0.02	0.0	0.0
	18-Apr	4.7	0.02	0.0	0.1
	19-Apr	4.5	0.01	0.1	0.1
C	13-Apr	8.5	0.01	0.0	1.0
	14-Apr	5.1	0.02	0.0	5.9
	15-Apr	2.8	0.02	0.0	5.3
	16-Apr	1.7	0.01	0.0	4.7
	17-Apr	1.3	0.02	0.0	4.5
	18-Apr	0.7	0.02	0.0	3.9
	19-Apr	0.5	0.02	0.0	3.7
D	13-Apr	6.4	0.03	0.0	1.0
	14-Apr	5.3	0.01	0.0	9.8
	15-Apr	4.5	0.02	0.1	13.0
	16-Apr	3.7	0.03	0.1	14.1
	17-Apr	3.7	0.02	0.2	15.7
	18-Apr	3.7	0.11	0.3	15.6
	19-Apr	3.6	0.01	0.2	16.9

B.5.2 Pilot-scale studies

B.5.2.1 Adsorption

B.5.2.1.1 Column A

Sample	Time (hr)	NH_3N_{avg} (mg/L)	STD DEV
$Feed_{init}$	0	25.8	0.10
$Feed_{final}$	24	26.0	0.16
2	0	0.2	0.01
3	1	0.1	0.00
4	4	0.1	0.01
5	5	0.1	0.01
6	6	0.1	0.01
7	9	0.4	0.01
9	11	1.5	0.01
10	12	2.2	0.02
11	14	4.5	0.03
23	16.8	7.3	0.04
14	17	7.6	0.04
15	18	9.0	0.03
16	19	11.1	0.08
17	20	12.5	0.05
18	21	13.8	0.05
19	22	15.1	0.00
20	23	16.5	0.10
21	24	17.4	0.10
22	24.5	18.0	0.16

B.5.2.1.2 Column B

Sample	Time (hr)	NH_3N_{avg} (mg/L)	STD DEV
$Feed_{init}$	0	25.8	0.12
2	0	1.9	0.01
3	1	0.2	0.00
4	2	0.1	0.01
5	3	0.2	0.00
7	5	0.2	0.00
9	7	0.2	0.00
11	9	0.2	0.00
13	11	0.2	0.01
15	13	0.2	0.00
17	15	0.2	0.01
19	17	0.3	0.01
21	19	0.3	0.00
23	21	0.2	0.01
24	22	0.3	0.00
25	23	0.3	0.01
26	24	0.5	0.01
27	25	0.6	0.01
28	26	0.7	0.01
1	27	0.9	0.00
E	27.47	1.1	0.00

B.5.2.1 Regeneration

B.5.2.1.1 Column A

Time (days)	pH	V_{eff} (mL)	NO_3N_{avg} (mg/L)	STD DEV	NH_4N_{avg} (mg/L)	STD DEV	N_{feed} (mg)	$Alk_{consumed}$ (mg/L as $CaCO_3$)
0.0	7.55	160	1.3	0.02	1.5	0.02	0.50	
0.9	7.55	105	16.0	0.04	3.7	0.02	0.33	
1.9	7.45	96	33.4	0.05	6.2	0.02	0.30	
2.8	7.40	103	40.5	0.08	6.6	0.04	0.32	
3.9	7.04	102	45.4	0.08	6.5	0.01	0.32	
4.8	6.91	97	45.0	0.08	6.2	0.02	0.30	
5.9	6.91	98	49.7	0.19	6.2	0.02	0.30	
6.8	6.56	96	47.2	0.08	5.8	0.02	0.30	
7.8	6.58	98	47.1	0.15	5.7	0.02	0.30	
8.8	6.72	96	50.5	0.15	5.7	0.04	0.30	
9.8	6.76	96	45.3	5.48	5.5	0.02	0.30	
10.8	6.23	100	48.3	0.08	5.3	0.03	0.31	260.9
13.8	6.90	736	37.3	0.08	5.1	0.03	2.28	
15.8	6.97	487	40.6	0.05	4.7	0.04	1.51	228.0
17.8	6.93	492	42.8	0.05	4.3	0.02	1.53	235.0
19.8	6.88	483	44.5	0.05	4.0	0.01	1.50	
21.8	6.68	492	43.5	0.00	3.7	0.00	1.53	
22.8	6.76	245	44.2	0.16	3.5	0.01	0.76	
25.8	6.83	715	44.0	0.05	3.4	0.01	2.22	
27.8	6.67	485	41.8	0.09	3.2	0.01	1.50	
29.8	7.14	481	43.1	0.05	3.1	0.01	1.49	229.9
31.6	7.35	588	35.4	0.64	2.6	0.01	1.82	234.2
35.6	7.09	1455	32.8	0.05	2.5	0.01	4.51	203.5
37.6	7.38	728	30.8	0.00	2.2	0.07	2.26	192.0
38.6	7.60	389	30.2	0.05	2.1	0.01	1.21	188.5
41.6	7.36	1042	30.3	0.05	1.8	0.01	3.23	188.2
43.6	7.32	758	28.2	0.12	1.7	0.01	2.35	170.6
45.6	7.48	718	28.7	0.08	1.5	0.01	2.23	187.0
48.6	7.56	1083	27.2	0.00	1.4	0.01	3.36	166.3
50.6	7.69	722	27.4	0.05	1.3	0.02	2.24	165.3
52.6	7.72	722	26.1	0.05	1.1	0.01	2.24	158.6
55.6	7.61	1077	24.3	0.09	1.0	0.02	3.34	150.7
57.6	7.87	718	23.1	0.08	0.9	0.01	2.23	137.7
59.6	7.60	714	23.6	0.05	0.8	0.01	2.21	138.2
62.6	7.82	1067	22.6	0.00	0.7	0.01	3.31	135.1

Time (days)	pH	V_{eff} (mL)	NO_3N_{avg} (mg/L)	STD DEV	NH_4N_{avg} (mg/L)	STD DEV	N_{feed} (mg)	$Alk_{consumed}$ (mg/L as $CaCO_3$)
64.6	7.69	717	22.2	0.30	0.7	0.01	2.22	128.2
67.6	7.70	1068	21.2	0.00	0.6	0.01	3.31	124.6
70.6	7.69	1069	21.7	0.21	0.5	0.02	3.31	115.1
73.6	7.78	1067	19.9	0.09	0.5	0.01	3.31	107.5
76.6	7.98	1061	18.1	0.05	0.4	0.01	3.29	99.0
80.6	7.93	1400	17.4	0.02	0.4	0.01	4.34	90.2
84.6	8.01	1411	15.8	0.08	0.4	0.01	4.37	
87.6	7.96	1044	15.1	0.05	0.3	0.01	3.24	73.0
91.6	8.05	1411	14.4	0.00	0.4	0.01	4.37	67.5
92.6	8.01	352	13.9	0.04	0.4	0.01	1.09	64.0
97.6	7.90	1864	10.1	0.05	0.3	0.01	0.47	49.3
104.6	7.64	2455	8.7	0.01	0.2	0.01	1.28	42.9
108.6	7.92	1440	7.8	0.01	0.3	0.02	0.87	32.6
112.6	7.92	1430	7.5	0.10	0.2	0.01	1.00	26.2
119.6	8.02	2503	6.7	0.01	0.2	0.01	2.45	15.3
126.6	7.82	2488	5.6	0.02	0.1	0.01	2.89	
133.6	8.19	2503	3.9	0.01	0.0	0.00	1.87	10.7
140.6	8.18	2528	2.6	0.01	0.0	0.00	2.77	12.5

B.5.2.1.2 Column B

Time (days)	V_{effl} (mL)	pH	NO_3N_{avg} (mg/L)	STD DEV	NH_4N_{avg} (mg/L)	STD DEV	NO_2N (mg/L)	$Alk_{consumed}$ (mg/L as $CaCO_3$)
0.8	222	7.56	55.5	0.12	1.9	0.01	0.0	160
1.8	234	7.25	40.3	0.00	0.8	0.00	0.1	176
2.8	239	7.12	38.3	0.16	0.5	0.01	0.1	191
5.8	701	6.94	39.4	0.00	0.5	0.01	0.0	203
6.8	235	0.00	39.4		0.5		0.0	
7.8	237	6.91	39.7	0.17	0.4	0.00	0.0	
8.8	235	6.96	39.3	0.09	0.4	0.01	0.0	214
10.8	466	6.66	39.5	0.05	0.4	0.00	0.0	217
13.8	704	6.76	39.8	0.05	0.4	0.02	0.0	217
15.8	573	7.10	39.2	0.27	0.5	0.01	0.0	217
16.8	230	6.84	40.7	0.08	0.5	0.00	0.0	223
19.8	708	6.93	39.0	0.09	0.4	0.00	0.0	222
20.8	233	6.93	39.0	0.09	0.3	0.01	0.0	
22.8	470	6.89	38.3	0.16	0.3	0.01	0.0	224
23.8	228	7.06	37.8	0.05	0.5	0.00	0.0	215
27.8	925	7.00	37.1	0.00	0.3	0.01	0.0	216
29.8	468	7.10	36.9	0.14	0.4	0.01	0.0	211
34.8	1146	7.13	36.9	0.95	0.4	0.02	0.0	209
35.8	229	7.17	34.2	0.05	0.4	0.01	0.0	203
36.8	231	7.39	34.5	0.48	0.3	0.02	0.0	200
42.8	590	7.32	42.0	0.05	0.4	0.00	0.0	204
43.8	230	7.44	30.8	0.12	0.2	0.03	0.0	200
47.8	918	7.39	31.6	0.14	0.2	0.01	0.0	180
51.8	924	7.57	29.7	0.09	0.2	0.01	0.0	163
55.8	900	7.55	27.1	0.05	0.1	0.01	0.0	148
57.8	440	7.85	25.7	0.05	0.1	0.00	0.0	129
62.8	1061	7.82	23.1	0.05	0.1	0.01	0.0	114
64.8	413	7.85	20.8	0.14	0.1	0.00	0.0	99
69.8	999	7.92	17.6	0.05	0.1	0.01	0.0	82
72.8	584	7.88	15.2	0.10	0.2	0.00	0.0	62
76.8	821	8.06	12.0	0.01	0.1	0.00	0.0	45
83.8	1515	8.10	9.4	0.03	0.2	0.01	0.0	21

B.5.2.1.3 Column B Feed

$Feed_{NH3N}$ (mg/L)	STD DEV	$Feed_{NO3N}$ (mg/L)	$Feed_{NO2N}$ (mg/L)
0	0.00	0.00	0.00
2.1	0.01	0.17	0.00
2.0	0.01	0.12	0.00
2.0	0.02	0.06	0.00
2.0		0.10	0.00
2.1	0.00	0.14	0.00
2.1	0.01	0.06	0.00
2.1	0.01	0.07	0.00
2.0	0.01	0.06	0.00
2.0	0.01	0.07	0.00
2.0	0.01	0.07	0.00
2.0	0.01	0.06	0.00
2.0	0.02	0.07	0.00
2.0	0.01	0.05	0.00
2.0	0.01	0.03	0.00
2.0	0.01	0.37	0.04
1.8	1.04	0.06	0.17
0.3	0.01	0.06	1.64
0.1	0.01	0.06	1.85
2.1	0.02	0.18	0.00
2.0	0.01	0.23	0.00
2.0	0.01	0.23	0.00
1.8	0.01	0.25	0.09
1.5	0.01	0.24	0.30
0.9	0.01	0.22	0.78
0.4	0.01	0.14	1.37
0.1	0.01	0.26	1.74
0.1	0.01	0.15	1.10
0.1	0.01	0.24	1.77
0.2	0.00	0.26	1.89
0.1	0.00	0.41	1.98
0.1	0.00	0.00	1.89

APPENDIX C. Wetland Design Example

APPENDIX C
WETLAND DESIGN EXAMPLE

This appendix outlines the procedure that could be used to design a constructed wetland-clinoptilolite bed treatment system. The constructed wetland design was taken from Reed *et al.* (1995). The process requires an iterative design and can more easily solved with a spreadsheet.

Problem Statement: Design a surface flow constructed wetland to treat a medium strength municipal waste (Tchobanoglous and Burton, 1991) with the following characteristics:

Contaminant	Influent Concentration	Effluent Target
BOD5 (mg/L)	220	30
SS (mg/L)	220	30
Total Nitrogen (mg N/L)	40	2
Organic	15	0
Ammonia	25	2

The system is needed for a lake community that will have an estimated flowrate of 10,000 gpd (40 m^3/d). The community is located in west central Indiana.

Solution:

Wetland Design

Step 1: Gather weather data for the location. There are several sources that can be used to gather the best available weather information. Temperature and precipitation data for Indiana can be found at http://shadow.agry.purdue.edu.

Month	Mean Temp. (°F)	Precipitation[a] (in)	Class A Pan Evaporation[a] (in)
January	24.2	2.04	0.00
February	28.2	1.99	0.00
March	40.0	3.40	0.00
April	51.5	3.89	3.57
May	61.9	4.25	6.45
June	71.1	3.91	7.31
July	74.7	4.47	7.39
August	72.4	3.95	6.13
September	66.0	3.15	4.80
October	54.1	2.74	3.41
November	42.5	3.32	1.32
December	30.0	3.14	0.00

[a]Values obtained by averaging precipitation and evaporation data from 1963 - 1993.

Step 2: Gather kinetic and design parameters for constructed wetland design equations. These parameters should be carefully considered by referencing the original source, the assumptions, and equations that were used in their development. As discussed earlier in this paper there are a variety of equations that can be used to design either a surface flow or subsurface flow constructed wetland. The wetland design presented in this appendix will be based on BOD and nitrogen removal; kinetic parameters are taken from Reed *et al.* (1995). The design equations for BOD removal are shown in Figure C.1, while the design equations used for nitrogen removal are found in Figure C.2.

Suspended solids (SS) removal is typically not a problem in constructed wetland systems, therefore it will not be considered in the design procedure. However, it should be checked after the design has been completed.

$$\frac{BOD_{out}}{BOD_{in}} = e^{-K_T t}$$

$$K_T = K_{20}\theta^{(T-20)}$$

$$t = \frac{V}{Q}$$

$$V = A_S dn$$

$$A_S = LW$$

Where :

A_S = surface area, m^2

L = length, m

W = width, m

d = depth, m

t = detention time, d

n = porosity, dec. fraction

T = temp, °C

Q = flowrate, m^3/d

K_T = temp. dependent 1^{st} – order rxn constant, 1/d

θ = temperature coefficient

Figure C.1: FWS wetland design equations for BOD removal (Reed *et al.*, 1995)

The following parameters were used for the BOD design:

$K_{20} = 0.2779\ d^{-1}$

$\theta = 1.06$

Porosity = 0.70 (Range 0.65 - 0.75)

Depth = 0.3 m (Range 0.1 - 0.46 m)

L:W ratio = 2 (range 1 - 10)

The following parameters were used for the nitrogen design:

$K_{20} = 0.2187\ d^{-1}$

$\theta = 1.048$

$$\frac{N_{out}}{N_{in}} = e^{-K_{TN}\Theta_H}$$

$$A_s = \frac{Q \ln\left(N_{in}/N_{out}\right)}{K_{TN}\, yn}$$

Where:

A_s = surface area of wetland, m^2

N_{in} = influent TKN conc., mg/L

N_{out} = effluent ammonia conc., mg/L

K_T = temp dependent rate constant

$= 0\ d^{-1}$ @ 0° C

$= 0.2187\,(1.048)^{(T-20)}\ d^{-1}$ @ 1° C+

n = wetland porosity, 0.65 - 0.75

θ_H = hydraulic residence time, d

y = water depth, m

Q = average flow, m^3 / d

Figure C.2: FWS wetland design equations for nitrogen removal (Reed *et al.*, 1995)

Step 3: Select thermal design parameters (see Figure C.3).

$$T_w = T_{air} + (T_0 - T_{air}) \exp\left[\frac{-U_s (x - x_o)}{\delta\, y\, v\, c_p}\right]$$

$$(x - x_o) = \frac{(\delta)(y)(v)(c_p)}{U_s}\left[\ln \frac{(3^\circ - T_{air})}{(T_o - T_{air})}\right]$$

$$T_w = T_m + (T_o - T_m) \exp - \left[\frac{U_i\,(x - x_o)}{(\delta)(y)(v)(c_p)}\right]$$

$$U_i = (\phi)\frac{(v)^{0.8}}{(y)^{0.2}}$$

Where:

T_w = water temp@ distance x, °C (°F), (x in m or ft)

T_{air} = avg air temp during period of interest, °C (°F)

T_m = ice melting point, 0° C (32° F)

T_0 = water temp at distance x_0, the entry point for the wetland segment of interest, °C (°F)

= water temp. at dist. x_o, where ice cover commences; assume 3° C (37.4° F)

U_s = heat transfer coefficient at wetland surface, $W/m^2 \cdot °C$, $(Btu/ft^2 \cdot h \cdot °F)$

$= 1.5\ W/m^2 \cdot °C$ (0.264 $Btu/ft^2 \cdot h \cdot °F$) for dense marsh vegetation

$= 10 - 25\ W/m^2 \cdot °C$ (1.761 – 4.403 $Btu/ft^2 \cdot h \cdot °F$) for open water, high

U_i = heat transfer coefficient at ice/water interface, $W/m^2 \cdot °C$, $(Btu/ft^2 \cdot h \cdot °F)$

δ = density of water 1000 kg/m^3 (62.4 lb/ft^3)

y = depth of water, m (ft)

v = flow velocity in wetland, m/s (ft/h)

c_p = specific heat, 4215 $J/kg \cdot °C$ (1.007 $Btu/lb \cdot °F$)

ϕ = proportionality coefficient

$= 1622\ J/m^{2.6} \cdot s^{0.2} \cdot °C$ (0.0022 $Btu/ft^{2.6} \cdot h^{0.2} \cdot °F$)

Figure C.3: Thermal design equations for surface flow constructed wetland. (Reed *et al.*, 1995)

The following parameters were selected:

$T_o = 21.1°C$ (70°F)

$U_s = 15\ W/m^2 \cdot °C$

Step 4: After all the parameters are selected start the design. Assume a minimum temperature for BOD removal in the coldest month. A good assumption is 3 °C. Use this to calculate K_T, t, A_s, v, W, and L. Assume that 2 cells will be built, and 40% BOD removal using a septic tank for pretreatment.

$$K_T = 0.10\ d^{-1}$$

$$t = 19.5\ d$$

$$A_{s,cell} = 1857\ m^2$$

$$W = 30.5\ m$$

$$L = 61\ m$$

$$v = 3.61 \times 10^{-5}\ m/s$$

Step 5: Calculate T_w for each month (Figure C.4) with the initial cell length; using the first equation in the thermal design equations. For any temperature that falls below 3 °C, calculate the distance at which the ice formation begins. Recalculate the effluent water temperature using the third equation from Figure C.3.

Step 6: Use the minimum temperature to recalculate the parameters in Step 4.

Monthly Calculations							
Month	*Avg Temp*[1]		*Tw*	*Ice*	*Freeze dist.*	*Tw*	*Regen/Adsorb*[2]
	(°F)	*(°C)*	*(°C)*	*Formation*	*(m)*	*(°C)*	
Aug	72.7	22.6	22.4				Regenerate
Sep	66	18.9	19.2				Regenerate
Oct	54.1	12.3	13.4				Regenerate
Nov	42.5	5.8	7.8				Adsorb
Dec	30	-1.1	1.8	Recalulate	51.1	2.6	Adsorb
Jan	24.2	-4.3	-1.0	Recalulate	37.6	2.2	Adsorb
Feb	28.2	-2.1	0.9	Recalulate	45.8	2.5	Adsorb
Mar	40	4.4	6.6				Adsorb
Apr	51.5	10.8	12.2				Regenerate
May	61.9	16.6	17.2				Regenerate
Jun	71.1	21.7	21.6				Regenerate
Jul	74.7	23.7	23.4				Regenerate

(1) WC division of IN
(2) Based on 10° C

Regeneration Months	7
Adsorption Months	5

Figure C.4: Spreadsheet results for thermal calculations .

Continue with Steps 4 & 5 until the cell length merges. The results from the iteration follows (Figures C.5, C.6, and C.7):

Inputs:

Q_{in} =	40	m^3/d	[influent flowrate from septic tank or sewage lagoon]
BOD_{in} =	140	mg/L	[from septic or sewage lagoon]
BOD_{out} =	20	mg/L	
K_{20} =	0.2779	1/d	[first-order reaction rate constant at 20°C; default = 0.2779]
n =	0.7		[porosity; range = 0.65-0.75; default = 0.7]
T =	2.2	°C	[temperature; default = 20]
⊖ =	1.06		[temperature dependent constant; default = 1.06]
y =	0.3	m	[depth of FWS wetland; range = 0.1 - 0.46; default = 0.3]
L:W ratio =	2		[length to width ration, range 1 - 10, default 2]
# of cells =	2		

Calculations:

Q_{cell} =	20	m^3/d	[to each cell]	
K_T =	0.0986	1/d		
$\ominus_H$ =	19.7	d		
A_{sl} =	1879	m^2	1.88	ha

Figure C.5: Spreadsheet results for BOD design.

Step 7: Design the SFW based on nitrogen removal. Calculate the wetland size necessary to reduce the effluent ammonia level to 2 mg/L during the coldest regeneration month. The temperature should be at least 10°C. The results of these calculations follow (Figure C.6):

	Input:	
Q_{in} =	40	
N_{in} =	40	mg/L
N_{out} =	2	mg/L
$K_{TN,20}$ =	0.2187	d-1
Θ_N =	1.048	
n =	0.7	
y =	0.3	mg/L
L:W ratio =	2	
# of cells =	2	
	Calculations:	
T_{min} =	13.4	°C
K_{TN} =	0.1608	d^{-1}
Θ_{HN} =	18.6	d
$A_{s,N}$ =	1774	m^2

Figure C.6: Spreadsheet results for nitrogen design.

Step 8: Compare the surface area required for nitrogen removal and BOD removal. Select the limiting surface area (Figure C.7). The final design is summarized from the spreadsheet:

Inputs

Q_{in} =	40	m^3/d	[influent flowrate from septic tank or sewage lagoon]
BOD_{in} =	140	mg/L	[from septic or sewage lagoon]
BOD_{out} =	20	mg/L	[effluent BOD]
K_{20} =	0.2779	1/d	[first-order reaction rate constant at 20°C for BOD removal; default = 0.2779]
⊙ =	1.06		[temperature dependent constant for BOD removal; default = 1.06]
Nin =	40	mg/L	[TKN from septic tank or lagoon]
Nout =	2	mg/L	[ammonia concentation in wetland effluent]
KTN,20 =	0.2187	d-1	
$⊙_N$ =	1.048		
n =	0.7		[porosity; range = 0.65-0.75; default = 0.7]
y =	0.3	m	[depth of FWS wetland; range = 0.1 - 0.46; default = 0.3]
L:W ratio =	2		[length to width ration, range 1 - 10, default 2]
# of cells =	2		

Limiting Nutrient = **BOD**
Controlling Surf. Area = **1879**

Width (m) = **30.7**

Area (m^2) =	1885 per cell
Volume (m^3) =	565 per cell
cells =	2
HRT (d) =	19.8
v (m/s) =	3.59E-05

Length (m) = **61.4**

Figure C.7: Spreadsheet results for final design calculations.

Clinoptilolite Bed Design

Step 9: Use the thermal data to determine the total number of adsorption months and the total number of bioregeneration months (see Step 6). Use 10°C the minimum temperature required for bioregeneration. There should be a minimum of 5 months available for regeneration.

Assume an effluent ammonia concentration of 25 mg/L for a medium strength municipal waste. Use an adsorption capacity of 1.9 mg NH_3N/g clinoptilolite. Therefore, the total mass of clinoptilolite required for a 6 month adsorption period is:

$$m_{clino} = \frac{Q_{in}\ NH_3N_{in}\ t}{\left(\frac{X}{m}\right)}$$

Where:

m_{clino} = mass of clinoptilolite (g)

Q_{in} = flowrate (m^3 / d)

NH_3N_{in} = ammonia conc. from wetland (mg / L)

t = adsorption period (d)

$\left(\frac{X}{m}\right)$ = solid phase conc. (mg $NH_4N_{adsorbed}$ / g clino)

$$m_{clino} = \frac{(40\ m^3/d)(25\ mg/L)(10^3\ L/m^3)(180\ d)}{(1.9\ mg/g)(10^3\ g/kg)}$$

$$\therefore m_{clino} = \underline{\underline{94700\ kg}}$$

Step 10: Calculate the bed size. Use a L:W ratio of 10:1 for the beds and a side wall slope of 2:1 (Vertical:horizontal). Construct at least two beds. The beds will be 1.3 m deep (~ 4 ft). The bulk density for St. Cloud 14-40 mesh is 784 kg/m^3.

The 4 beds should be connected so that they can be used in series for the adsorption phase of treatment.

$$V_{bed} = \frac{m_{clino}}{\gamma_{bulk}}$$

$$V_{bed} = \frac{94700\ kg}{784\ kg/m^3}$$

$$\therefore V_{bed} = \underline{\underline{121\ m^3}}$$

$$W = \sqrt{\frac{V_{bed}}{(\#\ of\ beds)(L:W)(d)}}$$

$$W = \sqrt{\frac{121\ m^3}{(4)(10)(1.3\ m)}}$$

$$\therefore W = \underline{\underline{1.5\ m}},\quad L = \underline{\underline{15.5\ m}}$$

Step 11: Determine the regeneration cycle. It takes 37 empty bed volumes (BV) of wetland effluent to regenerate the clinoptilolite bed. Also, assume that the void fraction in the beds is 0.35. The void volume for each bed is 10.6 m^3, for a total void volume of 42.4 m^3.

$$t_{regen} = \frac{V_{total}}{BV}\left(\frac{1}{Q_{regen}}\right)\left(BV_{regen}\right)$$

$$t_{regen} = \frac{121\ m^3}{BV}\left(\frac{1}{40\ m^3/d}\right)(37)$$

$$\therefore t_{regen} = \underline{\underline{112\ d}}$$

Based on this it would take the all of the flow from the wetland every day to regenerate the beds in 112 days. Note that one fill cycle for all four beds is approximately 1/3 BV.

Try regenerating 2 beds at 1.5 fill cycles/d or 3/4 Q. The regeneration time is:

$$t_{regen} = \frac{V_{total}}{BV}\left(\frac{1}{Q_{regen}}\right)\left(BV_{regen}\right)$$

$$t_{regen} = \frac{60.5\ m^3}{BV}\left(\frac{1}{30\ m^3/d}\right)(37)$$

$$\therefore t_{regen} = \underline{\underline{75\ d}}$$

Based on these calculations it would take 150 days to regenerate both beds. There are 180 days available for regeneration. If one used all 180 days the regeneration rate is 1.2 cycles/d. The wetland must be checked for evapotranspiration to ensure that enough effluent is available for regeneration.

The nitrate rich effluent from the clinoptilolite beds will be cycled back to the head of the wetland. This will almost double the flow, but the nitrate will reduce the incoming BOD load almost completely. The nitrate will be converted to nitrogen gas and emitted to the atmosphere.

DESIGN SUMMARY

Parameter	**Value**
Surface Flow Wetland	
Length (m)	61.4
Width (m)	30.7
Depth (m)	0.3
Number of Cells	2
Clinoptilolite Bed	
Length (m)	15.5
Width (m)	1.5
Depth (m)	1.3
Number of Cells	4
Regeneration Rate (cyc/d)	1.5 (regenerate 2 beds at a time)

VITA

VITA

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